VOL. XLII. JULY, 1909. No. 1.

AMERICAN

CHEMICAL JOURNAL

THE OXYGEN ETHERS OF THE DIALKYLUREAS.

BY RALPH H. MCKEE.

This paper is a contribution to our knowledge of the asymmetrical methyl (and ethyl) dialkylisoureas, $R_2N.COCH_3 = NH$, where R is CH_3, C_2H_5, C_3H_7, C_4H_9, or C_5H_{11}. These compounds were prepared and studied partly for comparison with the mother substance, methyl isourea, and with isoureas containing aromatic residues linked to nitrogen and other related compounds; and partly to serve as material for the study of certain typical organic reactions by the methods of physical chemistry.[1]

In general, it may be said that the methods of preparation and the reactions were much like those of the analogous aromatic substances which have been previously studied, except for differences due to the very much greater sensitiveness of the members of the present series to heat and reagents. In the preparation of the lowest member of the present series, methyl dimethylisourea, $(CH_3)_2N\text{-}COCH_3{=}NH$, the methods had to be much modified owing to its great volatility with ether and alcohol vapors, its complete miscibility with all solvents, and the rapid deliquescence and decomposition of its salts even at room temperature. The exact methods developed for the preparation of this new class of ethers, by the action of sodium alcoholate on the dialkylcyanamide, will be described in the experimental part.

---

[1] To be given in a later paper.

The basic oils obtained have densities which decrease as the alkyl radicals joined to nitrogen increase from methyl to isoamyl and are always less than that of water, the maximum density being about 0.97. The highest member, the isoamyl compound, is but slightly soluble in water, one part in 1500, but the solubility increases as we go down the series until, with methyl dimethylisourea, we find complete solubility in every ratio with all common solvents. The intermediate members show the unusual phenomenon of being several times as soluble in cold water as in warm water. The substances are strong enough bases to affect the skin in the same manner as a solution of potassium hydroxide, to dissolve aluminium hydroxide, and to give perfectly neutral salts with one equivalent of the strong acids. The only slightly soluble salt which has been found for any of these bases is the one formed with hydroferrocyanic acid. This acid also gives, with the isoureas containing aromatic residues linked to nitrogen, slightly soluble salts which, as well as those described in the present paper, are acid salts containing but one molecule of the base to one of the acid.

The hydrochlorides are readily precipitated by the addition of dry hydrogen chloride to the cold ether or ligroin solution of the base. On heating these hydrochlorides, methyl chloride and the urea are formed quantitatively according to the equation

$$R_2N\text{-}COCH_3{=}NH.HCl = R_2N\text{-}CO\text{-}NH_2 + CH_3Cl.$$

Even at room temperature, this reaction readily takes place, *e. g.*, methyl diisoamylisourea hydrochloride practically completely decomposed in three months in this manner. Methyl dimethylisourea hydrochloride is but slightly more stable.

On heating a water solution of a hydrochloride at 100°, the same decomposition into a dialkylurea and alkyl chloride was found to occur quickly. Hitherto, it has been considered that alkyl chloride splits off the easier the more negative the groups attached to nitrogen, but the hydrochlorides of this series have the most basic alkyls possible joined to nitrogen and yet give alkyl chloride far more easily than the analogous aromatic bodies. One of the more interesting new developments is that this formation of alkyl chloride and urea, on heating the water solution of the hydrochloride, is found to be a decomposition of the unionized portion and is not a reaction in which the ions take part.

Heated with water, the higher members react but slowly, the lower members more rapidly (65 per cent in two hours at 100°), but in each case the reaction seems to proceed simply and completely according to the equation

$$R_2N\text{-}COCH_3{=}NH + H_2O = R_2N\text{-}CO\text{-}NH_2 + CH_3OH,$$

with no evidence of the formation of ammonia and a urethane.

By heat alone, *i. e.*, without a solvent, the lower members are decomposed into the cyanamide and alcohol from which the isourea was originally prepared.

EXPERIMENTAL PART.

Methyl Diisobutylisourea (*Methyl Diisobutylimidocarbamate*), $(C_4H_9)_2N.C(:NH)OCH_3$.—The preparation of this isourea from diisobutylcyanamide[1] was attempted, but without success, according to the method by which Lengfeld and Stieglitz[2] brought about the addition of alcohol to carbodiimide, *i. e.*, by heating in sealed tubes. In no case was any alkaline oil formed by heating the cyanamide with absolute alcohol, though temperatures varying from 100° to 225° were tried.

A moderate degree of success attended the attempt to bring about the addition of alcohol by the method used by Pinner[3] in the preparation of imidoethers from acid nitriles and by which I have prepared isoureas containing aromatic residues linked to nitrogen.[4] Diisobutylcyanamide (1 mol.) was dissolved in absolute alcohol (10 mol.) and dry hydrogen chloride (1 mol.) slowly run into the resulting solution, kept cold by ice. After standing a week at room temperature, dilution with water no longer brought about the separation of an oil, unchanged diisobutylcyanamide, and the action was considered to be complete. The excess of alcohol was removed by evaporation in a vacuum over sulphuric acid and solid caustic potash. Crystals of the hydrochloride separated in fair amount. These were washed with ether and, after recrystallization from ethyl acetate, analyzed by titration with standard silver nitrate. 0.3088 gram required 13.74 cc. 0.1 N silver nitrate (chromate indicator); calculated for $(C_4H_9)_2N.C(:NH).OCH_3.HCl$, 13.86 cc. By treatment of the hydrochloride with caustic potash, the free methyl diisobutylisourea was obtained. The method gives about sixty per cent of the possible yield, calculated from the cyanamide taken, but requires much time for the completion of the reaction and the isolation of the hydrochloride. The time taken by the reaction may be shortened to several hours by heating the mixture to 40°–50°, but this hastening of the reaction is accompanied by some decomposition of the hydrochloride formed.[1]

---

[1] McKee: This Journal, **36**, 210 (1906).

[2] Ber. d. chem. Ges., **27**, 926 (1894).

[3] Imidoäther und ihre Derivate (1892), page 3.

[4] Stieglitz and McKee: Ber. d. chem. Ges., **32**, 1495 (1899); **33**, 808 (1900). McKee: This Journal, **26**, 215 and ff. (1901).

The method finally found to give the best results, with a minimum of expenditure of material and time, was that of adding the diisobutylcyanamide (1 mol.) to a solution of sodium (1.1 atoms) in dry methyl alcohol (10 mol.).[2] The resulting solution was either kept at room temperature a week or, more commonly, the completion of the reaction hastened by heating at 55° for two hours. To the mixture, cooled below 15°, dilute hydrochloric acid was added until the reaction was almost neutral, and any unchanged diisobutylcyanamide was removed by extraction with ether. The hydrochloric acid solution was then treated with an excess of a strong solution of potassium hydroxide, the oil which separated taken up with ether, the ether solution washed several times with small amounts of water, and dried with anhydrous sodium sulphate. After distilling off the ether, the oil was distilled in a vacuum. The yield of pure substance was equal to the weight of the cyanamide taken.

---

[1] When the hydrochloride of the isourea to be prepared is sufficiently stable towards heat, this shortening of the time can often be used with considerable advantage, *e. g.*, the time for the completion of the reaction by which methyl isourea (Stieglitz and McKee: Ber. d. chem. Ges., **33**, 1517 (1900)) is formed from cyanamide may be shortened from several days to about half an hour, if a temperature of 40° is used. A decrease in the amount of alcohol from 25 to 2 molecules for each molecule of cyanamide used was found not to decrease the yield, but only to lengthen the time at 40° from 0.5 hour to 2.5 hours. Similarly, in the preparation of methyl phenylisourea, an hour's heating at 40° is equivalent to several days' standing at room temperature (McKee: This Journal, **26**, 228 (1901)). Cf. Bruce: J. Am. Chem. Soc., **26**, 423 (1904).

[2] Cf. McKee: This Journal, **36**, 209 (1906).

An attempt to replace the sodium methylate solution by an alcoholic solution of potassium hydroxide was only partially successful, the yield of the isourea being but forty per cent of the calculated.

Methyl diisobutylisourea is a colorless oily liquid having a basic, somewhat fishy odor. It boils at 102° (14 mm.), 116° (22 mm.), 135° (42 mm.), and with some decomposition at 218°–222° (742 mm.). I was not able to effect the crystallization of the oil. Titration of the oil with standard acid showed it to be a strong monacid base. With methyl orange, 0.4928 gram required 26.44 cc. 0.1 N hydrochloric acid; calculated for $C_{10}H_{22}N_2O$, 26.45 cc. Density at 18.5°, referred to water at 4° (Westphal), 0.8933. It is readily soluble in all the ordinary organic solvents and slightly so in water, the resulting solution being strongly alkaline. Its solubility is greater in cold than in warm water. An approximate determination of its solubility by titration, with 0.1 N acid, of the saturated solution gave the following results: 1.14 parts at 0°, 0.94 parts at 10°, 0.61 parts at 21°, 0.49 parts at 30°, and 0.32 parts at 85° in 100 parts of water.

The imidoethers have been shown qualitatively to give, when heated in a current of dry hydrogen chloride, alkyl chloride and the acid amide. The similarity of the oils under discussion was shown in an experiment where dry hydrogen chloride was passed over 0.38 gram methyl diisobutylisourea in a test tube connected with an azotometer filled with 20 per cent sodium hydroxide solution.

At 0°, there was little action except that of absorption of the hydrogen chloride. On heating, there began at 45° a slow evolution of gas, which did not perceptibly increase until 95° was reached, two-thirds of the gas evolved being obtained between 95° and 100°. In all there was obtained 43 cc. of a gas which was not absorbed by caustic soda and which burned with a green-tinged flame, showing it to be methyl chloride. The difference of 3 cc. between the volume of methyl chloride obtained, 43 cc., and the volume calculated, 46 cc., according to the equation

$$(C_4H_9)_2NC(:NH)OCH_3 + HCl = (C_4H_9)_2N.CO.NH_2 + CH_3Cl,$$

is probably due to the solubility of methyl chloride in the sodium hydroxide solution used in the azotometer.

In addition to proving the quantitative formation of methyl chloride, the presence of diisobutylurea, or rather its hydrochloride, in the residue was demonstrated and thus the reaction expressed by the above equation was shown to be the exclusive one. A solution of the residue in a little cold water gave, with an aqueous solution of oxalic acid, a precipitate, which, after drying on a porous plate, melted at 114°–115° with evolution of gas. The melting point was unchanged when mixed with diisobutylurea oxalate[1] synthesized for comparison. The picrate was prepared by dissolving some of the residue in a little water, making the resulting solution slightly alkaline with ammonium hydroxide to remove the hydrochloric acid present, and adding a solution of picric acid in dilute alcohol. After drying on a porous plate, the salt melted at 90°, and when mixed with the synthetic urea picrate (see below), melting at 90°–91°, the melting point was unchanged.

Methyl Diisobutylisourea Hydrochloride, $(C_4H_9)_2N.C(:NH)OCH_3.HCl$.—Dry hydrogen chloride was passed into a solution of the isourea in cold absolute ether, the precipitated hydrochloride filtered off, and, after washing with ether, dried *in vacuo* over caustic potash and sulphuric acid.

Methyl diisobutylisourea hydrochloride is insoluble in ether and ligroin, slightly soluble in cold, but readily soluble in boiling benzene and ethyl acetate, and very soluble in water and alcohol. It may be recrystallized from hot ethyl acetate. When heated, it gives methyl chloride and the urea.

---

[1] Page 8.

Methyl Diisobutylisourea Ferrocyanide, $(C_4H_9)_2N.C(:NH)OCH_3.H_4Fe(CN)_6$.—In an attempt to obtain an easy scheme of identification for the isoureas, the salts of a large number of acids were made. All of these were found to be extremely soluble, and consequently difficult to purify, except the acid ferrocyanides. These ferrocyanides did not, however, give the definite and characteristic melting points desired.

On adding a solution of ferrocyanic acid[1] to methyl diisobutylisourea, no precipitation took place until enough had been added to make the solution distinctly acid. There then appeared a very fine white precipitate of the acid salt[2] containing one molecule of the base to one of the acid. This salt is so insoluble that the filtrate does not become blue on treatment with ferric chloride. It seems to be stable at room temperature, but when heated to 100° in an air bath, there is decomposition with the formation of an ill-smelling vapor (isonitrile?) and a darkening in color of the salt.

An analysis for iron, by moistening with sulphuric acid and igniting, gave 13.54 and 13.55 per cent iron; calculated for $C_{16}H_{26}ON_8Fe$, 13.89 per cent.

Diisobutylurea, $(C_4H_9)_2N.CO.NH_2$, is not described in the literature and so was prepared in order that its properties might be known and the identity of the product formed by methyl diisobutylisourea, when heated with hydrogen chloride or with hydrochloric acid, be made certain.

Diisobutylamine was neutralized with dilute hydrochloric acid and caused to react with an equivalent amount of potassium isocyanate by heating on a water bath. The viscous oil which separated was taken up with ether. The resulting ethereal solution was washed with water, dried with fused calcium chloride, and the ether removed by distillation. The oil distilled at about 180° (25 mm.) without decomposition. It is more soluble in cold than in warm water, the resulting solutions reacting neutral to litmus. It is readily soluble in all the ordinary organic solvents. Crystallization was started by rubbing some of the oil with a few drops of water. Inoculation of the remainder of the oil gave crystals which, after drying on a porous plate, melted at 72°–74°.

---

[1] Baeyer and Villiger: Ber. d. chem. Ges., **34**, 2687 (1901).

[2] Similar slightly soluble ferrocyanides are formed by ethyl diphenylisourea, methyl phenylmethylisourea, ethyl phenylisourea, methyl dipropylisourea and methyl *p*-tolylisourea. The corresponding salts of methyl phenylisourea and ethyl isourea are readily soluble and that of methyl dimethylisourea is only moderately soluble. Ferricyanic acid gives similar salts but they are all somewhat more soluble. The salts of both acids are much more soluble in alcohol than in water.

Attempts to prepare a crystalline nitrate were without success. However, it was found to form slightly soluble crystalline salts with picric acid and oxalic acid.

Diisobutylurea Oxalate, $[(C_4H_9)_2N.CO.NH_2]_2.H_2C_2O_4$, was precipitated as flat four-sided prisms on mixing aqueous solutions of the urea and oxalic acid. It melts at 115° with evolution of a gas. Analysis was made by titration with standard alkali and phenolphthalein. 0.1959 gram required 8.98 cc. 0.1 N potassium hydroxide; calculated for $C_{20}H_{42}O_6N_4$, 9.02 cc.

Diisobutylurea Picrate, $(C_4H_9)_2N.CO.NH_2.C_6H_2(NO_2)_3OH$, was prepared by the addition of a solution of picric acid in dilute alcohol to an aqueous solution of the urea. It separated as an oil which, on being cooled and rubbed with a glass rod, became crystalline. It was filtered off, washed with a little water, and dried on a porous plate. Microscopic needles melting at 90°–90°.5. Dissolved in warm water, cooled, and inoculated with some of the crystals previously obtained, it melted at 90°–91°. It melts without decomposition, for, after allowing it to solidify in the melting point tube, a second heating gave the same melting point. Its composition was made certain by titration with 0.1 N potassium hydroxide and phenolphthalein. 0.4684 gram required 12.15 cc.; calculated for $C_{15}H_{23}O_8N_5$, 11.67 cc.

Action of Dilute Hydrochloric Acid on Methyl Diisobutylisourea.—In the presence of dilute acid, the imidoethers are readily hydrolyzed according to the equations

$$\text{(I)}\ RC(:NH)OCH_3 + HCl + H_2O = RCOOCH_3 + NH_4Cl \text{ or}$$
$$\text{(II)}\ RC(:NH)OCH_3 + HCl + H_2O = RCO.NH_2 + CH_3OH + HCl.$$

Phenylisourea ethers[1] have been shown to decompose without hydrolysis according to the equation

$$\text{(III)}\ C_6H_5NH.C(:NH)OCH_3 + HCl + H_2O = C_6H_5NH.CO.NH_2 + CH_3Cl + H_2O.$$

With the unsubstituted isourea, $NH_2.C(:NH)OCH_3$, while the main reaction is according to (III), with formation of urea and methyl chloride, there is formed at the same time a little urethane[2] according to an equation analogous to (I):

$$\text{(IV)}\ NH_2.C(:NH)OCH_3 + HCl + H_2O = NH_2.COOCH_3 + NH_4Cl.$$

In the study of the action of dilute acid on dialkylisoureas of the type of methyl diisobutylisourea, it was early shown that the principal action, at 100°, was analogous to that with the phenylisourea ethers, *viz.*, a decomposition into alkyl chloride and the urea according to the equation

$$\text{(V)}\ (C_4H_9)_2N.C(:NH)OCH_3 + HCl + H_2O = (C_4H_9)_2N.CO.NH_2 + CH_3Cl + H_2O,$$

water having taken no part in the reaction.

The attempt to determine if this was the only kind of decomposition undergone was made difficult by the fact that, under the conditions of the experiment, the urea first formed is rapidly hydrolyzed with formation of diisobutylamine, ammonia, and carbon dioxide:

$$(C_4H_9)_2N.CO.NH_2 + H_2O = (C_4H_9)_2NH + CO_2 + NH_3.$$

The diisobutylamine set free by the hydrolysis of the urea is a strong base and takes a part of the hydrochloric acid unto itself, thereby reducing the amount of the isourea present as the hydrochloride. When the reactions of the amyl member are described, it will be shown that the formation of methyl chloride is due to the decomposition of the unionized isourea hydrochloride.

One and twenty-two hundredths grams of methyl diisobutylisourea hydrochloride[3] were dissolved in 2.5 cc. water and the resulting solution, approximately 1.5 N, was heated in a test tube in a boiling water bath. The gas evolved was collected in an azotometer filled with 20 per cent sodium hydroxide. In four hours, gas had ceased to be evolved and the contents of the test tube had become strongly alkaline, due to the diisobutylamine formed by hydrolysis of diisobutylurea. A little hydrochloric acid was added to the contents of the tube and the whole heated for an hour longer. This caused the evolution of 28 cc. more methyl chloride, and made a total of 124 cc. (20° and 745 mm.), equivalent to 111 cc. (0° and 760 mm.). For 1.22 grams of the hydrochloride, if the decomposition into the urea and alkyl chloride is quantitative, the calculated amount of methyl chloride is 121 cc. (0° and 760 mm.). The solubility of methyl chloride in the aqueous sodium hydroxide accounts, at least in large part, for the 10 cc. discrepancy between the volume found and that calculated for a quantitative decomposition into the urea and alkyl chloride.

---

[1] McKee: This Journal, **26**, 219 (1901).

[2] *Ibid.*, **26**, 250 (1901).

[3] Page 6.

The gas was identified as methyl chloride by its burning with a green-edged flame. The oil which had separated in the tube was identified as the urea by the abundant precipitate melting at 115° which it gave with oxalic acid. This melting point was not changed when the substance was mixed with the synthetic diisobutylurea oxalate[1] melting at 115°. It likewise gave a picrate melting at 90°–91°, which, when mixed with the synthetic diisobutylurea picrate, still melted at 90°–91°.

That there was no urethane formation was shown by the lack of the odor characteristic of the urethanes, $(C_4H_9)_2N.COOAlk$, and by the fact that a definite and sharp end point was obtained when the hydrochloride solution, after being heated, was made neutral to methyl orange by 0.1 N acid. It will be shown below that the substituted urethanes have a characteristic odor and are so distinctly basic that, in their presence, a base cannot be titrated to a sharp neutrality point.

Methyl Diisobutylcarbamate (*Diisobutylmethylurethane*), $(C_4H_9)_2N.CO_2CH_3$, was synthesized in order to obtain accurate knowledge of its properties and obviate any likelihood of overlooking its presence, in even small amounts, if it had been formed by the action of dilute acid or of water on the isourea. It was prepared by adding an ethereal solution of diisobutylamine (1 mol.) to a slight excess (1.2 mol.) of twenty per cent potassium hydroxide and then, with vigorous shaking after each addition, slowly adding to the resulting mixture, kept below 10°, an ethereal solution of methyl chlorcarbonate. The ethereal and aqueous layers were separated, and the former, after being washed with dilute acid and water, was dried with fused calcium chloride.

---

[1] Page 8.

The oil remaining after distilling off the ether boils at 204° (753 mm.). The yield is excellent. It is readily soluble in the ordinary organic solvents and slightly in water. It is readily soluble in concentrated sulphuric acid and from this solution is precipitated unchanged on the addition of water. It has a persistent and characteristic odor similar to that given by the analogous dipropyl- and dimethylurethanes.

That it is slightly basic was shown by treating three drops of the oil with 30 cc. water, a drop of methyl orange solution, and adding 0.1 N acid from a burette. About 0.20 cc. more acid was required to pass through the neutral tints, *i. e.*, from the point where the pink *began* to appear until a clear pink, free from yellow, was obtained, than in a parallel experiment with distilled water.

This somewhat basic character of the urethane was shown even more plainly by a comparison of its solubility in water and acids. The determinations were made by filling a previously calibrated Babcock milk bottle with the solvent and then adding about half a cubic centimeter of the oil. The volume of the oil was read exactly by the divisions on the neck, and the bottle corked and shaken well for thirty minutes. Rotation in the centrifugal machine now caused the undissolved oil to collect in the neck. The volume was again read and the decrease gave the volume of the oil dissolved in the amount of solvent taken. No account was taken of the possible increase in volume of the oil due to the solution of water in the oil. Its effect would be very slight and in any case affect the several determinations almost equally. At 18°, this urethane, methyl diisobutylcarbamate, was found to require approximately 4000 parts water, 1200 parts dilute (3 N) hydrochloric acid, and 200 parts concentrated (12 N) hydrochloric acid for solution.

That the basic character found is not peculiar to this substance nor due to an impurity, but is common to this class of oils, was shown by a careful examination of the effect of several other urethanes on the neutrality of methyl orange and by comparisons of their solubilities in water and in dilute and concentrated acids.

Ethyl Diisobutylcarbamate (*Diisobutylurethane*), $(C_4H_9)_2N.COOC_2H_5$.—The ethyl ester was prepared from ethyl chlorcarbonate, by the method just described for methyl diisobutylcarbamate, with a yield of 90 per cent of the calculated amount. It boils at 100° (13 mm.) and 203° (757 mm.). In its odor, solubilities, and slightly basic character, as shown by titration with standard acid and methyl orange, it is very similar to the methyl ester. Determination of its solubility at 17° by the centrifugal method gave the following results: one part of ethyl diisobutylcarbamate dissolves in 320 parts, by volume, concentrated (12 N) hydrochloric acid, 640 parts dilute (3 N) hydrochloric acid, and 1600 parts of water.

That the greater solubility in acid is not due to hydrolysis of the oil by the acid was shown when a bottle containing the strong acid and the urethane was well shaken, kept overnight lying on its side, in order to insure thorough contact of the oil with the acid, and the next day the volume of the urethane, remaining undissolved, redetermined. The volume of the oil had not decreased by an amount greater than the error of reading, 0.006 cc.

Action of Water on Methyl Diisobutylisourea.—One and twenty-five hundredths grams of methyl diisobutylisourea, with ten times that weight of water, were heated at 100° in a sealed tube for 11 hours. The tube opened with no pressure. The contents of the tube were carefully transferred to a separatory funnel and titrated with normal hydrochloric acid and methyl orange. 4.42 cc. were required; calculated for 1.25 grams isourea if no decomposition had taken place, 6.67 cc. The end point was perfectly sharp, indicating the absence of slightly basic substances like diisobutylurethane or diisobutylcyanamide. The absence of these possible reaction products was made certain by the fact that the methyl orange solution did not change color, *i. e.*, become more acid, when the solution was shaken with ether. Diisobutylurethane, $(C_4H_9)_2NCOOCH_3$, and diisobutylcyanamide, $(C_4H_9)_2NCN$ are weak bases slightly soluble in water and very soluble in ether and as such would be largely extracted by the ether from the water solution and leave the latter more acid. No change of the neutrality point could be detected. The water solution was extracted three times with ether and the ether extract washed with water, dried with granular calcium chloride, and evaporated, leaving a residue of yellowish oil. This oil was dissolved in two cubic centimeters of alcohol and a saturated aqueous solution of oxalic acid added in excess. The crystals which separated weighed 0.48 gram and melted at 110°. Recrystallized, they melted at 115° alone, and when mixed with the synthetic diisobutylurea oxalate[1]. Forty-eight hundredths gram of the urea oxalate is equivalent to a decomposition of 0.41 gram of the isourea according to the equation

$$(C_4H_9)_2N.C(:NH)OCH_3 + H_2O = (C_4H_9)_2N.CO.NH_2 + CH_3OH.$$

The titration with acid would indicate that 0.42 gram of the isourea had reacted according to the above equation. The agreement of these two determinations is partially due to two errors of measurement being in opposite directions and apparently of about equal amounts. The first is that the weight of the oxalate obtained is undoubtedly low to the extent of its solubility in the dilute alcohol solution from which it was precipitated. The second error is due to the fact that there is some hydrolysis of the diisobutylurea:

$$R_2N.CO.NH_2 + H_2O = R_2NH + NH_3 + CO_2;$$

which, increasing the alkalinity of the solution, reacts in the titration to decrease the apparent amount of isourea decomposed. Each of these errors is very small and there seems to be no reason for doubting that the isourea reacts with water to form only diisobutylurea and methyl alcohol. It is thus seen that the action of water is simple and entirely analogous to the action previously shown qualitatively with the isoureas[1] and imidoethers.[2]

---

[1] Page 8.

Action of Benzoyl Chloride on Methyl Diisobutylisourea.—It has been shown[3] that the monophenylated oxygen ethers of urea, $C_6H_5NH.C(:NH)OCH_3$, can be benzoylated quite readily without the loss of the alkyl group attached to oxygen, the reaction proceeding along the same lines as with the imidoethers which contain a replaceable hydrogen atom attached to nitrogen. Dains,[4] with the symmetrical diphenylated isoureas, $C_6H_5NH.C(:NC_6H_5)OAlk$, found that acyl chlorides reacted with the formation of alkyl chloride and a trisubstituted urea, a reaction quite different from that mentioned above, but entirely analogous to that found by Wheeler and Walden[5] to occur when imidoethers having no hydrogen directly bound to the nitrogen are acted upon by acyl chlorides.

With the isoureas described in the present paper, the action with acyl chlorides was found to be exclusively a replacement of the imide hydrogen by the acyl group according to the equation

$$(C_4H_9)_2N.C(:NH)OCH_3 + ClCOC_6H_5 = (C_4H_9)_2N.C(:NCOC_6H_5)OCH_3 + HCl,$$

with no evidence of urea and methyl chloride formation. In other words, the reaction is entirely analogous to that obtained with the monophenylated isoureas and the ordinary imidoethers and shows no similarity to that of Dains's diphenylisoureas, or Wheeler and Walden's imidoethers of the type $RN:CH.OC_2H_5$.

Methyl diisobutylisourea was treated, in the presence of an excess of ten per cent caustic potash solution, with an equivalent amount of freshly distilled benzoyl chloride dissolved in absolute ether. At 5°, the reaction was complete in ten minutes. The ethereal layer was removed, washed with one per cent acid to remove any unchanged methyl diisobutylisourea, and with water, and then dried with anhydrous sodium sulphate. Evaporation of the ether *in vacuo*, over concentrated sulphuric acid, left the methyl benzoyldiisobutylisourea as a viscid colorless oil, corresponding in amount to 92 per cent of the calculated. It is readily soluble in ether, chloroform, and alcohol, and slightly in ligroin, insoluble in water and in strong sodium hydroxide solution.

---

[1] McKee: This Journal, **26**, 218 (1901).
[2] Wheeler: *Ibid.*, **17**, 398 (1897).
[3] McKee: This Journal, **26**, 226 (1901).
[4] J. Am. Chem. Soc., **21**, 181 (1899).
[5] This Journal, **19**, 130 (1898).

When 0.41 gram of the oil was gradually heated to 100° in a tube, in a current of dry hydrogen chloride, there was some evolution of gas even at 20°, but the evolution of gas did not become vigorous until the temperature approached 50°. The volume of methyl chloride obtained in the azotometer, which had been filled with 20 per cent sodium hydroxide, was only 3 cc. less than the calculated, an amount which was probably entirely due to the solubility of methyl chloride in the aqueous sodium hydroxide used. The residue in the tube was found to contain benzoyl chloride, identified by its odor and that of the ester formed by heating it with alcohol, thus indicating that the benzoyldiisobutylurea first formed had, under the action of the excess of hydrogen chloride, decomposed to some extent. No attempt was made to identify the other products formed. That benzoyl chloride actually is formed on heating benzoyldiisobutylurea[1] under these conditions was shown in a supplementary experiment where the urea alone was subjected to the action of hydrogen chloride and heat.

Action of Dilute Hydrochloric Acid on Methyl Benzoyldiisobutylisourea.—Though containing the strongly negative benzoyl group, methyl benzoyldiisobutylisourea, when heated at 100° with dilute acid, was found to react in a manner perfectly analogous to that observed with the other isoureas, *i. e.*, quantitative decomposition into methyl chloride and urea took place on heating the oil with an equivalent of normal hydrochloric acid. The experiment was carried out by attaching the test tube, containing the isourea and acid, by means of a capillary tube to a Lunge nitrometer and measuring the amount of methyl chloride evolved when the test tube was heated in a boiling water bath. The urea, after one crystallization from 50 per cent alcohol, melted at 121°–122°; mixed with pure benzoyldiisobutylurea (see below), it melted 0°.5 higher.

---

[1] Page 16.

Methyl Benzoyldiisobutylisourea Hydrochloride, $(C_4H_9)_2N.C(:NCOC_6H_5)OCH_3.HCl$, was precipitated when a solution of the isourea, in low boiling ligroin, was cooled to −15° by a freezing mixture, and treated with dry hydrogen chloride. It first separated as an oily film which, in a few minutes, became crystalline. The solid was filtered off, washed with cold (−10°) ligroin, and then transferred to a porous plate. In a minute it had become pasty and in another minute it had changed to a viscous oil and was rapidly giving off bubbles of a gas. This gas burned with a green-edged flame and was probably methyl chloride. The material remaining on the porous plate was a solid which, after crystallization from 50 per cent alcohol, was identified by its melting point and solubilities as benzoyldiisobutylurea (see below). It is thus evident that a hydrochloride is formed but that at room temperature it rapidly decomposes into alkyl chloride and the urea.

Benzoyldiisobutylurea, $(C_4H_9)_2N.CO.NHCOC_6H_5$.—An attempt was first made to synthesize this urea by benzoylating diisobutylurea, in pyridine solution, but without success. The urea was prepared by dissolving the corresponding isourea in absolute ether, adding an excess of dry hydrogen chloride, and then allowing the ether to evaporate at room temperature, the hydrochloride first formed decomposing with formation of the urea. After three crystallizations from 50 per cent alcohol, the urea melted at 123°–123°.5 without decomposition. It is insoluble in cold water, slightly in hot water, but readily in ether and alcohol and caustic alkali solution. From the latter it is precipitated unchanged by the addition of acid. From 50 per cent alcohol it crystallizes as thick rhombic plates. Analysis: 0.1539 gram gave 0.3931 gram CO_2 and 0.1200 gram H_2O.

	Calculated for $C_{16}H_{24}O_2N_2$.	Found.
C	69.50	69.66
H	8.77	8.74

Methyl Diisoamylisourea (*Methyl Diisoamylimidocarbamate*), $(C_5H_{11})_2N.C(:NH)OCH_3$, was prepared from diisoamylcyanamide[1] and sodium methylate, by the same method as was used in the preparation of the diisobutylisourea. The yield is excellent. Methyl diisoamylisourea boils at 125° (7 mm.), 133° (12 mm.), and 153° (30 mm.). It is readily soluble in the common organic solvents, but is only soluble in 1500 parts water at 15°. Its density is 0.8860 at 18°, referred to water at 15° (Westphal). Titrated with 0.1 N hydrochloric acid and methyl orange 0.4413 gram required 20.39 cc.; calculated for $C_{12}H_{26}ON_2$, 20.59 cc.

Methyl Diisoamylisourea Hydrochloride, $(C_5H_{11})_2N.C(:NH)OCH_3.HCl$.—This salt was prepared by precipitation at 10° from the ligroin solution of the isourea with hydrogen chloride. The salt was dried in a vacuum over solid potassium hydroxide and paraffin. It was found to melt, with evolution of a gas, at 104°. An analysis was made by titration with standard silver nitrate solution, using chromate indicator: 0.3516 gram required 14.03 cc.; calculated, 14.02 cc.

The salt decomposes spontaneously on being kept at room temperature; in six weeks it was more than one-third decomposed and in three months the decomposition was almost complete. The product left was an oil which was identified as diisoamylurea by its oxalate melting at 102° alone, and also when mixed with the synthetic diisoamylurea oxalate (see below).

Diisoamylurea, $(C_5H_{11})_2N.CO.NH_2$.—This urea was prepared by warming a solution of the amine sulphate with an equivalent amount of potassium isocyanate. The oil which separated was taken up with ether, and the ethereal solution washed with very dilute acid and water and dried. Evaporation of the ether left an oil which could not be made to crystallize.

---

[1] McKee: This Journal, **36**, 210 (1906).

The urea did not give a slightly soluble nitrate. Its picrate was slightly soluble but did not crystallize. Oxalic acid added to a solution of the urea in very dilute alcohol at once gave a crystalline precipitate. The crystals of the oxalate are four-sided prisms having dome ends and melting at 102.°5 with evolution of a gas. 0.6662 gram required 27.04 cc. 0.1 N sodium hydroxide, with phenolphthalein as indicator; calculated for $[(C_5H_{11})_2N.CO.NH_2]_2H_2C_2O_4$, 27.15 cc.

Action of Dilute Hydrochloric Acid on Methyl Diisoamylisourea.—Methyl diisoamylisourea heated with an equivalent of normal hydrochloric acid gave methyl chloride in quantity and an oil lighter than water. The oil was identified as diisoamylurea by its oxalate melting at 102°.5 alone and when mixed with the synthetic urea oxalate. The contents of the tube gave a sharp end point to methyl orange and 0.1 N acid, thus indicating that no urethane or diisoamylcyanamide had been formed.

Measurements of the rate of evolution of methyl chloride from solutions of various concentrations and in the presence of a substance having a common ion indicate that the reaction is one of the first order and due to the decomposition of the unionized hydrochloride and is not a reaction in which the ions take a part. Exact measurements of the percentage of ionization of the salt and rate of the decomposition into methyl chloride and diisoamylurea are under way and the results will be published shortly.

Ethyl Diisoamylisourea (*Ethyl Diisoamylimidocarbamate*), $(C_5H_{11})_2N.C(:NH)OC_2H_5$, was prepared in the same way as methyl diisobutylisourea. It boils at 158° (28 mm.). A water solution of the isourea blackens mercurous chloride and gives a white precipitate with a solution of mercuric chloride. The character of these mercury compounds has not yet been investigated.

Certain work by Bruce[1] was thought to favor the view that the silver salt of methyl phenylisourea has the formula

---

[1] J. Am. Chem. Soc., 26, 435 (1904).

$C_6H_5NH.C(:NAg)OCH_3$ rather than the formula $C_6H_5NAg.C(:NH)OCH_3$ which would be expected from Bamberger's work[1] in which he showed that in the salts of phenylamidines the silver probably goes to the amide group. If, in the metallic salts of the isoureas, the metal is in the amide group then there is no reason why an isourea like $(C_5H_{11})_2N.C(:NH)OC_2H_5$, which has a replaceable imide hydrogen, should not give metallic salts, but if, on the other hand, these salts can only have the metal in the amide group, then such an isourea as the one just mentioned could not give a metallic salt. Attention may be called to the fact that all the isoureas which have been described in the literature[2] as giving metallic salts have a free hydrogen atom in the amide group.

Numerous attempts to prepare sodium, potassium, and silver salts of ethyl diisoamylisourea, by various modifications of the methods which have been previously used, were all without success. In no case was there any heat evolution or absorption, separation of a solid containing nitrogen, or any other evidence of salt formation, thus furnishing additional evidence in favor of the Bamberger view of the composition of such metallic salts.

Ethyl Diisoamylisourea Hydrochloride, $(C_5H_{11})_2N.C(:NH)OC_2H_5.HCl$.—Ethyl diisoamylisourea was dissolved in absolute ether and dry hydrogen chloride passed into the solution kept below 10°. At first there was no separation of a solid, but after a minute or two, a fine mush of microscopic needles separated. The crystals were washed on the pump with absolute ether and dried *in vacuo* over caustic potash and sulphuric acid.

The salt is extremely soluble in water, the resulting solution being neutral to sensitive litmus. It melts at 125° with evolution of ethyl chloride. From the slowness with which the precipitation from the ether solution occurred when the salt was being prepared one would expect it to be distinctly soluble in ether. A determination of its solubility showed that 3.59 parts dissolve in 100 parts absolute ether at 17°. It is insoluble in ligroin. A chlorine determination was made by titration with 0.1 N silver nitrate and chromate indicator. 0.3712 gram required 14.02 cc.; calculated for $C_{13}H_{29}ON_2Cl$, 14.02 cc.

---

[1] Ann. Chem. (Liebig), **273**, 277 (1893).

[2] McKee: This Journal, **26**, 232 (1901). Bruce: J. Am. Chem. Soc., **26**, 434 (1904).

Methyl Dipropylisourea (*Methyl Dipropylimidocarbamate*), $(C_3H_7)_2N.C(NH)OCH_3$, was prepared by the general method[1] used with the other isoureas of this series.

Attempts to prepare sodium and silver salts were all unsuccessful, as were the similar experiments with ethyl diisoamylisourea which have just been described. Solutions of mercurous and mercuric salts gave with water solutions of this isourea black and white precipitates of the same appearance as those given by ammonia. The character of these complex salts has not been investigated.

Some of the isourea heated in a current of hydrogen chloride gave an almost quantitative yield of methyl chloride. A little of the alkyl chloride was set free below 20° but gas evolution did not become decided until about 100°; the tube was not heated above 104°. A water solution of the residue left in the tube gave with oxalic acid an oxalate melting at 102°–103° which, when mixed with the synthetic dipropylurea oxalate,[2] melted at the same temperature. With picric acid a picrate melting at 136° was obtained. As this is one degree higher than the melting point of the asymmetrical dipropylurea picrate as given by Zande[3] the picrate was synthesized by his method and found to melt at 136°. Its identity was made certain by a titration with standard alkali and phenolphthalein; exactly the calculated amount was required to neutralize it.

Methyl Dipropylisourea Hydrochloride, $(C_3H_7)_2N.C(:NH)OCH_3.HCl$, was prepared by precipitation of the ether solution of the base with dry hydrogen chloride. Unlike the corresponding diethyl- and dimethylisourea hydrochlorides, to be described later, it is not appreciably deliquescent. That it decomposes readily at room temperature was shown by a titration with silver nitrate and chromate indicator, three days after preparation, giving 17.97 per cent chlorine, and a second titration, a month later, 16.59 per cent; calculated for $C_8H_{19}ON_2Cl$, 18.21 per cent.

---

[1] Page 4; This Journal, 36, 209 (1906).

[2] Chancel: Bull. Soc. Chim. [3], 9, 103 (1893).

[3] Rec. Trav. Chim., 8, 224 (1889).

Action of Hydrochloric Acid on Methyl Dipropylisourea.—Methyl dipropylisourea hydrochloride, dissolved in double its weight of water, was heated at 100° for 1.5 hours. The sealed tube opened with considerable pressure due to methyl chloride. The contents of the tube, after heating, were neutral to methyl orange, thus showing the absence of any urethane formation by water taking part in the reaction.[1] The dialkylurethanes, $(C_3H_7)_2NCOOCH_3$ and $(C_3H_7)_2NCOOC_2H_5$, are weak bases giving indefinite end points with methyl orange and other indicators (see just below). The contents of the tube, when treated with oxalic acid, gave an abundant precipitate of the needle crystals of dipropylurea oxalate melting at 103°.

A second experiment, where the conditions were the same except that the temperature was 55° for 4.2 hours, showed a distinct but only very slight decomposition into dipropylurea and methyl chloride.

In a third experiment where the tube was kept at room temperature for two years the change into dipropylurea and methyl chloride had proceeded only to about the same extent as in the experiment where the tube was heated at 55° for 4.2 hours. The small amount of decomposition of the aqueous solution of the hydrochloride at 20° is somewhat surprising in view of the rate of decomposition of the dry salt at the same temperature shown just above.

Methyl Dipropylcarbamate (*Dipropylmethylurethane*), $(C_3H_7)_2N.COOCH_3$, was prepared in the same manner as methyl diisobutylcarbamate.[2] Yield, 82 per cent. It boils at 191° (751 mm.). In its odor and indefinite neutrality point when treated with methyl orange and 0.1 N acid it closely resembles the urethanes previously described. It is much more soluble in cold water than in warm water. Approximate determinations of its solubilities at 18° by the centrifugal method[1] showed that one part, by volume, dissolves in 300 parts water, and in 160 parts of dilute (3 N) hydrochloric acid. It is readily soluble in all the ordinary organic solvents and in the concentrated acids, and from the last it is precipitated unchanged by the addition of water.

---

[1] Page 9, Equation (IV).

[2] Page 10.

Ethyl Dipropylcarbamate (*Dipropylurethane*), $(C_3H_7)_2N.COOC_2H_5$.—The method of preparation, solubilities, and other properties of the ethyl ester are very similar to those of the methyl ester which has just been described. It boils about 200° (749 mm.).

Ethyl Dipropylisourea (*Ethyl Dipropylimidocarbamate*), $(C_3H_7)_2N.C(:NH)OC_2H_5$, was prepared by the same method as the methyl ester except that sodium ethylate was used instead of sodium methylate. It boils at 92° (10 mm.). As might be expected the reactions and properties are entirely similar to those which have been described for the methyl ester.

Stability of Ethyl Dipropylisourea.—It will be shown later that methyl dimethylisourea and ethyl isourea, when heated at 100°, are decomposed into the cyanamide and alcohol originally used in the preparation.

Heated for 50 hours at 100° ethyl dipropylisourea does not appreciably decompose. This was shown by the facts that there was no change in the boiling point; that the distillate from a solution of the oil in dilute hydrochloric acid failed to give the iodoform test for alcohol; that a titration with 0.1 N acid required for neutrality the amount of acid which would be required for the pure ethyl dipropylisourea; and that the end point to methyl orange in the above titration was sharp, thus showing the absence of even traces of dipropylcyanamide.

Methyl Dimethylisourea (*Methyl Dimethylimidocarbamate*), $(CH_3)_2N.C(:NH)OCH_3$.—The first attempts to prepare this isourea from dimethylcyanamide by the use of sodium methylate, according to the method used so successfully with the higher members of the series, gave evidence that the isourea had been formed but it was found impossible to separate it from the solvent by fractional distillation even when the fractionation was carried out at reduced pressure. Addition of gaseous hydrochloric acid and evaporation in a vacuum of the alcoholic solution was very tedious nor did it give the pure salt desired. Passing over the numerous attempts which met with only partial success we will describe the method which finally gave the pure substance. In general it may be said that the difficulties arose from the isourea being soluble in every ratio in water and all organic solvents and that its salts, in so far as tried, were deliquescent and extremely soluble in water and alcohol and decomposed on standing at room temperature.

---

[1] Page 11.

Five and six-hundredths grams sodium (1.1 atoms) were dissolved in absolute methyl alcohol and the excess of alcohol boiled off until only about 25 grams (4 mol.) of the alcohol remained. To the cold mush of crystals of sodium methylate 14 grams (1 mol.) of dimethylcyanamide[1] were added. A clear yellowish solution resulted which, in about half a minute, became hot (80°), and needles of sodium methylate, $NaOCH_3.CH_3OH$ separated. The flask was cooled under the faucet to moderate the reaction. After standing 20 minutes there was added 100 cc. ether, a little methyl orange, and then, very carefully, and with thorough cooling with ice, concentrated hydrochloric acid drop by drop until the indicator gave a permanently acid reaction. Strong potassium hydroxide (1 : 2) was then added to the extent of 0.5 cc. more than needed to make the solution neutral. On removal and evaporation of the ethereal layer some unchanged dimethylcyanamide was recovered. The aqueous layer was extracted twice more with ether and the resulting extracts discarded. The aqueous solution was then treated with 100 cc. ether and solid caustic potash until no more would dissolve. Some cooling of the vessel was necessary during the addition of the caustic potash. The extraction of the saturated caustic potash solution with ether was repeated twice more and the combined ether extracts, after drying with solid caustic potash, distilled at reduced pressure.

---

[1] A still better method of preparation of this material than that previously described by the author in THIS JOURNAL, **36**, 211 (1906), was found to be as follows: To dimethylamine hydrochloride (1 mol.) was added about one-eighth its weight of water and considerable ether. The flask was cooled and powdered caustic potash (2.5 mol.) added. A solution of bromcyanogen (1 mol.) in three times its weight of ether was then added in portions, the contents of the flask, kept cold by ice water, being well shaken between the additions. When the bromcyanogen had all been added, the ethereal layer was removed and, after the addition of calcium chloride to remove water and a little potassium cyanide to remove any excess of bromcyanogen, the ether was distilled off from the solution and the impure dimethylcyanamide fractioned. Eighty per cent of the dimethylamine hydrochloride taken was changed into the cyanamide desired. The conditions essential for a good yield seem to be a low temperature, a small amount of water, some excess of caustic potash, and dilute solutions of the substances reacting in ether.

Methyl dimethylisourea boils at 60.°5 (27 mm.), 86° (98 mm.), and, with slight decomposition, at 146.°5 (755 mm.). This is about 38° lower than the unsubstituted mother substance, $NH_2C(:NH)OCH_3$.[1] Density of a not quite entirely pure specimen at 16.°5, referred to water at 4°, was 0.9708 (Westphal). Exposure to the air produced no apparent change except that due to evaporation.

Titration with 0.1 N hydrochloric acid and methyl orange gave slightly low results, but perhaps as close as could be expected considering the nature of the substance. In order to avoid loss by evaporation the weighing was made in a glass bulb and a glass bottle used for the titration, the bulb, after the addition of water, methyl orange, and a part of the acid, being broken with a heavy glass rod. 0.2405 gram required 23.09 cc. and 0.1295 gram required 12.38 cc. 0.1 N acid; calculated for $C_4H_{10}ON_2$, 23.55 cc. and 12.67 cc.

Its concentrated water solution gives the skin the same soapy feeling as a solution of potassium hydroxide. When dissolved in a little water there is a distinct heat evolution which would lead to the inference that, like methyl dipropylisourea, it is more soluble in cold than in warm water. However I was not able, by heating the concentrated (1:2 and 1:1) water solutions, to bring about a separation of the base as a distinct layer which would disappear on cooling, and thus verify this inference.

A water solution of the isourea dissolves silver oxide and aluminium hydroxide but not cupric hydroxide. With a solution of mercuric chloride it gives a white precipitate soluble in an excess of the isourea, and with mercurous nitrate a black precipitate similar in appearance to that given by ammonia. The nature of these salts has not been determined.

---

[1] Stieglitz and McKee: Ber. d. chem. Ges., **33**, 1518 (1900).

Action of Water on Methyl Dimethylisourea.—In general it may be stated that, at 100°, the reaction with water gave exclusively dimethylurea and methyl alcohol and no trace of the corresponding urethane or cyanamide. At room temperature the action was slow and there was, in addition to the same products as were formed at 100°, some evidence of the formation of a trace of dimethylurethane or dimethylcyanamide. The experimental portion, which follows, was made as nearly quantitative as possible.

The solution (1:2) of the isourea in water, when titrated with standard acid, was found to contain 0.323 gram of the isourea in each cubic centimeter. Two cc. of this solution in a sealed tube were heated in a boiling water bath for two hours. The tube opened with no pressure and the odor of the isourea was still plain. Titration of 1 cc. required 11.43 cc. of 0.1 N acid for neutrality. This would correspond to 0.118 gram of the unchanged isourea remaining in 1 cc. of the solution.[1] The end point, with methyl orange as the indicator, was quite definite, thus showing that neither dimethylcyanamide, $(CH_3)_2NCN$, nor dimethylurethane, $(CH_3)_2N.COOCH_3$, were present in appreciable amounts. Separate experiments have shown that dimethylcyanamide and dimethylurethane give indefinite end points with methyl orange and 0.1 N acid.

To the remainder (1 cc.) of the solution was added an excess of an alcoholic solution of picric acid, the tube cooled to 10°, and the precipitate filtered off and dried on a porous plate. It weighed 0.40 gram and melted at 133° alone and when mixed with the synthetic dimethylurea picrate.[2] The filtrate from the dimethylurea picrate had a volume of 4.5 cc., of which all except 1 cc. was alcohol. A solubility determination showed that 100 parts dilute alcohol (70 per cent) containing a little picric acid dissolves about 4 parts dimethylurea picrate, or 0.18 gram for the 4.5 cc. of the filtrate. This amount (0.18 gram) added to the weight of the picrate precipitate (0.40 gram) obtained above corresponds to 0.187 gram methyl dimethylisourea. This added to the unchanged isourea found by titration (0.118 gram) gives 0.305 gram which is, within the limit of error of the measurements, the weight of the isourea taken (0.323 gram) in each cubic centimeter.

---

[1] Possibly this alkalinity is due in part to ammonia and dimethylamine formed by hydrolysis (cf. page 13) of the dimethylurea, but with the short time of heating, this factor is so very small that it has been disregarded.

[2] Zand [Rec. Trav. Chim., **8**, 224 (1889)] describes α,α dimethylurea picrate as melting at 130°, but I found that, if carefully prepared and not washed too much on the filter (water readily hydrolyzes the salt) it melts at 133°.

When the action of water at room temperature was studied it was found that with a solution of the same strength the reaction was the same in general character as at 100° but required about a month for half completion. At the end of a month the titration with tenth-normal acid and methyl orange required one more drop of acid for the completion of the color changes at the neutrality point than it should have done if nothing but methyl alcohol and dimethylurea had been formed. Evidently there had been formed a trace of a slightly basic substance like dimethylcyanamide or more probably, judging from the analogies between the isoureas and imidoethers,[1] dimethylurethane. Dimethylcyanamide would be formed by the loss of alcohol from the isourea molecule, and dimethylurethane by the addition of water and the loss of ammonia. With the quantities of material at hand I was not able to suggest a method by which the trace of the slightly basic substance could be isolated and completely identified.

Methyl Dimethylisourea Hydrochloride, $(CH_3)_2N.C(:NH)OCH_3.HCl$, was prepared by adding dry hydrogen chloride to a cold solution of methyl dimethylisourea in either absolute ether or ligroin. The salt first separated as an oil but by scratching with a glass rod this was caused to crystallize in four-sided needles. The salt was dried *in vacuo* over caustic potash and concentrated sulphuric acid. Analyses for chlorine showed 25.52 and 25.56 per cent; calculated for $C_4H_{11}ON_2Cl$, 25.58 per cent. Heated rapidly it melted at 91° with gas evolution and the residue in the melting point tube solidified and on further heating remelted at 174°-175°.[1]

---

[1] McKee: THIS JOURNAL, **26**, 258 (1901). Pinner. Die Imidoäther und ihre Derivate (1892), pages 6 and 7.

The hydrochloride must be handled very quickly for it takes up moisture from the air as rapidly as fused calcium chloride. It is very soluble in all the ordinary solvents except ether and ligroin. Attempts to recrystallize it by the addition of ether, or ligroin, to its concentrated alcoholic solution, or to a solution in chloroform, were all without success.

A nearly pure sample of the hydrochloride was kept in a desiccator over concentrated sulphuric acid and solid potassium hydroxide for some months. By titration of weighed amounts from time to time with silver nitrate it was found that there was a steady loss of chlorine—in eight months the percentage of chlorine decreased from 25.5 to 3.4 per cent. A careful examination of the material left after eight months' standing by precipitating the concentrated aqueous solution with alcoholic picric acid, according to the method earlier used,[2] showed that the amount of dimethylurea present exactly accounted for the weight of material taken, if allowance were made for an amount of the unchanged isourea hydrochloride corresponding to the 3.4 per cent chlorine found still present in the material. In other words the reaction at room temperature is fairly rapid and is *exclusively* a decomposition into dimethylurea and methyl chloride.

The identity of the dimethylurea picrate obtained above was made certain by its melting point (133°)[3] and by titration with 0.1 N alkali and phenolphthalein. 0.5766 gram required 18.09 cc. sodium hydroxide; calculated for $C_9H_{11}O_8N_5$, 18.17 cc.

Stability of Methyl Dimethylisourea.—Pinner has shown[4] that the imidoethers slowly decompose at room temperature, and more quickly on heating, into the nitrile and alcohol from which they were originally prepared. With the isoureas no similar decomposition has been detected. I now find that an analogous decomposition actually takes place in a few cases.[1]

---

[1] Franchimont [Rec. Trav. Chim., 3, 222 (1884)] gives the melting point of the asymmetrical dimethylurea as 180°.

[2] Page 25.

[3] Footnote, page 25.

[4] *Loc. cit.*

Three and nineteen-hundredths grams methyl dimethylisourea were heated in a sealed tube at 100° for 50 hours. The tube opened with no pressure. A small amount of a solid insoluble in ether had separated. The amount of this solid was so small (0.07 gram) that its identification was not found to be practicable.

Some of the oil, after decantation from the solid, was dissolved in dilute acid and the resulting solution half distilled. The distillate gave a strong test for methyl alcohol when treated with a hot copper spiral and resorcinol.[2] A parallel test with the original isourea did not give this reaction for methyl alcohol.

Titration of 0.2452 gram of the oil required 21.11 cc. 0.1 N acid; calculated for the unchanged isourea, 24.00 cc. The neutrality point to methyl orange was not sharp, indicating that dimethylcyanamide, a weak base, had been formed according to the equation

$$(CH_3)_2N.C(:NH)OCH_3 = (CH_3)_2N.CN + CH_3OH.$$

Owing to the closeness of their boiling points, their great volatility with ether vapor, and the similarity of their solubilities, it is not possible to separate a small amount of dimethylcyanamide from the isourea. An indirect proof of its presence was obtained by preparing more of the isourea from it and determining the amount of the methyl dimethylisourea formed by the increased alkalinity. This was accomplished by mixing some of the oil, in which it was desired to show the presence of dimethylcyanamide, with a little of a three-fourths normal solution of sodium methylate in methy alcohol, titrating 1 cc. with standard acid, heating for an hour at 45°, and then titrating again. The increase in alkalinity was due to the formation of methyl dimethylisourea from the dimethylcyanamide and accounted for more than two-thirds of the discrepancy between the acid used, 21.11 cc., and the calculated amount, 24.00 cc., in the first-mentioned titration of the oil.

---

[1] But not in all cases: cf. page 22.

[2] Mulliken and Scudder: This Journal, **21**, 266 (1889).

A parallel experiment with ethyl isourea, $NH_2.C(:NH)OC_2H_5$, showed that the decomposition is very much more rapid but entirely analogous to that just described for the dimethylisourea, except that there is a polymerization of one of the primary products of the reaction. Ethyl isourea heated at 100° for 2.5 hours in a sealed tube gave much solid mixed with a little liquid. The filtrate largely boiled at 78° and gave the iodoform test for ethyl alcohol. Ethyl isourea does not give the iodoform reaction.

The solid after crystallization from hot water was analyzed by titration with 0.1 N hydrochloric acid and methyl orange. 0.1610 gram required 12.24 cc., 0.1028 gram required 7.90 cc.; calculated for melamine, $(NH_2CN)_3$, 12.76 cc. and 8.15 cc. The point of neutrality of the titration was uncertain to about 0.10 cc. of the acid used. That it was melamine was made entirely certain by its solubilities and by the fact that by heating it in a dry tube it gave at low heat a white sublimate and at a higher temperature ammonia gas and a yellow residue (mellon).

A test for dicyandiamide[1] showed that substance to be present in small amounts. Parallel experiments showed that neither the isourea nor the melamine give this violet color with copper sulphate.

The reaction at 100° seems then to be a decomposition of the isourea according to the equation

$$NH_2.C(:NH)OC_2H_5 = NH_2CN + C_2H_5OH,$$

and then the customary polymerization of the unstable cyanamide to form some dicyandiamide, $(NH_2CN)_2$, but principally melamine, $(NH_2CN)_3$.

The study of these compounds is being continued.

LAKE FOREST COLLEGE,
LAKE FOREST, ILLINOIS;
April 20, 1909.

---

[1] Bamberger and Seeberger: Ber. d. chem. Ges., **26**, 1587 (1893).

[Contributions from the Sheffield Laboratory of Yale University.]

CLXVII.— RESEARCHES ON PYRIMIDINES: THE PREPARATION OF 3-METHYL- AND 3-BENZYLURACIL.

[FORTY-THIRD PAPER.]

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

From a theoretical standpoint a larger number of alkyl compounds may result by alkylating a uracil derivative than can be obtained by a similar treatment of a 2-mercapto-6-oxypyrimidine. With the mercaptopyrimidines only three mono-derivatives should result. With uracil, 4-methyluracil, thymine, or 5-methyluracil, in each case there are ten possible compounds, four mono- and six dialkyl derivatives. This includes oxygen derivatives, but not tautomeric forms. In the case of the 2-amino-6-oxypyrimidines, the guanidine derivatives, the alkylation may be still more complicated.

The work done in this laboratory has therefore been confined almost entirely to the alkylation of mercaptopyrimidines. 2-Ethylmercapto-6-oxypyrimidine[1] and 2-ethylmercapto-5-ethoxy-6-oxypyrimidine[2] gave with potassium hydroxide and methyl iodide the 1-methyl derivatives in largest quantity, while 2-ethyl-mercapto-5-methyl-6-oxypyrimidine[3] gave a mixture of about equal amounts of the 1- and 3-methylated products. 2-Ethylmercapto-5-ethoxy-6-oxypyrimidine[4] with benzyl chloride also gave a 1-benzyl derivative as the chief product.

On the other hand 2-ethylmercapto-6-oxypyrimidine[5] and 2-ethylmercapto-5-methyl-6-oxypyrimidine gave mostly 3-alkyl compounds with benzyl chloride. A similar result was obtained with the former pyrimidine and ethyl chloracetate.[6]

Besides the N isomers there were probably formed, in most of these cases, some 6-oxyalkyl derivatives (oils), the amount

[1] Johnson and Heyl: THIS JOURNAL, **37** 628 (1907).

[2] Johnson and Jones: *Ibid.*, **40**, 538 (1908).

[3] Johnson and Clapp: J. Biol. Chem., **5**, 51 (1908).

[4] Johnson and Jones: *Loc. cit.*

[5] Johnson and Derby: THIS JOURNAL, **40**, 444 (1908).

[6] Wheeler and Liddle: J. Am. Chem. Soc., **30**, 1152 (1908).

of 6-oxy derivative being noteworthy in the methylation of 2-anilino-6-oxypyrimidine.[1]

These examples show that no regularity is observed in the alkylation of 2-mercapto-6-oxypyrimidines, that analogous salts can give different results with the same halide, and that with different halides the salts may be attacked in different positions. It will also be noticed from the above that the papers so far published have contained accounts only of the results obtained with 2-mercapto-6-oxypyrimidines. It was therefore of interest to study the alkylation of some isomeric 2-oxy-6-mercaptopyrimidines and to examine the effect produced when the mercapto group and the oxygen atom were interchanged.

We now find when 2-oxy-6-methyl-mercaptopyrimidine (V.) is treated with potassium hydroxide, in alcoholic solution, and either methyl iodide or benzyl chloride, that 3-alkyl derivatives result. The amount of isomeric products, if any, formed in this reaction is very small.

The 6-mercapto derivatives, like the 2-mercapto compounds, on boiling with hydrochloric acid evolve mercaptan and pass smoothly into uracil derivatives. The new 3-methyluracil (VII.) thus obtained now completes the list of the theoretically possible monomethyluracils. It gives no color with diazobenzenesulphonic acid although the isomeric 1-methyluracil gives a red coloration.[2]

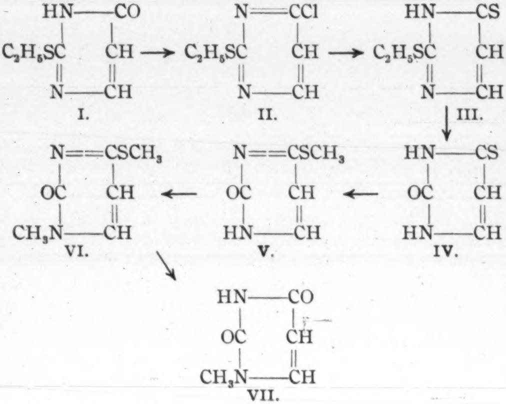
2-Oxy-6-methylmercaptopyrimidine (V.) was prepared by methylating 6-thiouracil (IV.), while the preparation of the latter substance has been described by Wheeler and Liddle.[3] The various steps in the synthesis of 3-methyluracil may be represented as follows:

---

[1] Johnson and Heyl: THIS JOURNAL, **38**, 238 (1907).

[2] Johnson and Clapp: J. Biol. Chem., **5**, 163 (1908)

[3] THIS JOURNAL, **40**, 547 (1908).



3-Methyluracil dissolves in alkali and is precipitated unaltered by hydrochloric acid.

Müller[1] obtained a 3-methyluracil-4-carboxylic ester by condensing oxalacetic ethyl ester and methylurea. When the sodium salt of this substance was treated with hydrochloric acid he obtained β-methyluramidoacrylic acid, $H_2N - CO - N(CH_3)CH = CHCOOH$. Neither acids nor alkalies changed this substance into 3-methyluracil.

Similar peculiar relations have been observed before in the pyrimidine series. Fischer and Roeder[2] in their synthesis of uracil obtained an acid which differed from uracil by one molecular proportion of water. It was left undecided whether this substance was uracilic acid (Uracilsäure), $H_2N - CO - NHCH = CHCOOH$, or oxyhydrouracil,

$\overbrace{HN - CO - NH - CH_2 - CHOHCO}$. They did not succeed in converting the substance into uracil.

Johnson and Clapp[3] obtained two α-methyl-β-guanidineacrylic acids. One could be dissolved in dilute alkali and be reprecipitated by acids unaltered, with the other this treatment closed the ring and gave 2-amino-5-methyl-6-oxypyrimidine. The explanation given for the existence of these two acids was that they represented the *cis* and *trans* modifications.

---

[1] J. prakt. Chem., **56**, 498 (1897).

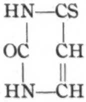
[2] Ber. d. chem. Ges., **34**, 3760 (1901).

[3] This Journal, **32**, 130 (1904).

Such an explanation might also account for the fact that—like Müller's pyrimidines—certain uracil derivatives dissolve in alkali and on precipitating with acids give the corresponding uramidoacrylic acids, while others—such as our 3-methyluracil—are precipitated in the form having the closed, uracil ring.

EXPERIMENTAL PART.

The preparation of 2-ethylmercapto-6-thiopyrimidine from 2-ethylmercapto-6-chlorpyrimidine[1] has been described by Wheeler and Liddle.[2] In the present work instead of employing two and a half times the calculated quantity of potassium hydrosulphide we have taken four times the calculated amount. By this method a yield of over 90 per cent of the calculated quantity of 2-ethylmercapto-6-thiopyrimidine was obtained.



$$\begin{array}{ll} HN- & CS \\ | & | \\ OC & CH \\ | & \| \\ HN- & CH \end{array}$$

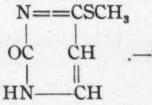
6-Thiouracil, .—When 2-ethylmercapto-6-thiopyrimidine is treated with concentrated hydrochloric acid the pale yellow color of the compound changes to a bright yellow. If water is added the color disappears or becomes much lighter. If this solution is boiled too long the material is completely desulphurized and uracil is obtained. The following procedure, however, gave a yield of over 90 per cent of the calculated amount of 6-thiouracil: Nine and six-tenths grams of 2-ethylmercapto-6-thiopyrimidine were added to a mixture of 50 cc. of concentrated hydrochloric acid and 50 cc. of water. On warming, mercaptan was evolved and solution took place, then 6-thiouracil separated. The acid was evaporated on the steam bath and the residue was crystallized from water.

---

[1] Wheeler and Johnson: THIS JOURNAL, **29**, 496 (1903); **31**, 596 (1904).

[2] *Ibid.*, **40**, 555 (1908).

2-Oxy-6-methylmercaptopyrimidine,

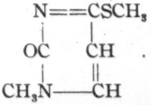


$$\begin{array}{lcl} \mathrm{N} & = & \mathrm{CSCH_3} \\ | & & | \\ \mathrm{OC} & & \mathrm{CH} \\ | & & \| \\ \mathrm{HN} & - & \mathrm{CH} \end{array}$$

.—One and one-tenth grams of sodium were dissolved in 25 cc. of methyl alcohol and 6.1 grams of 6-thiouracil were added. The mixture became semisolid owing to the separation of a colorless, difficultly soluble sodium salt. Ten grams of methyl iodide and 25 cc. more methyl alcohol were added. On warming the mixture, solution soon took place and it then gave a neutral reaction. The alcohol was evaporated and the residue was treated with water. Crystalline material separated which, after washing with water and drying, weighed 5 grams, or 73.7 per cent of the calculated. This dissolved easily in hot water and on cooling, long, slender needles or prisms were obtained melting to an oil with no effervescence at 205°.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.71	19.50

2-Oxy-3-methyl-6-methylmercaptopyrimidine,



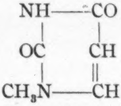
$$\begin{array}{lcl} \mathrm{N} & = & \mathrm{CSCH_3} \\ | & & | \\ \mathrm{OC} & & \mathrm{CH} \\ | & & \| \\ \mathrm{CH_3N} & - & \mathrm{CH} \end{array}$$

.

—Four and four-tenths grams of sodium were dissolved in 100 cc. of absolute alcohol and then 10.5 grams of 6-thiouracil were added. On warming a clear solution resulted. The solution was then cooled and 28 grams of methyl iodide were added. A mass of colorless crystals consisting of the sodium salt of 2-oxy-6-methylmercaptopyrimidine separated. On adding 100 cc. more of alcohol and warming for a few hours a clear solution that had a neutral reaction was again obtained. The alcohol was then evaporated off, the final portions in a vacuum. The product was separated from sodium iodide by repeated extractions with chloroform. When about 9.5 grams of material had been extracted it was purified by crystallizing from benzene. It separated in needles which melted at 124° to a clear oil without effervescence.

It was very soluble in cold water, alcohol, chloroform, and boiling ethyl acetate.

	Calculated for $C_6H_8ON_2S$.	Found.
N	17.95	17.76

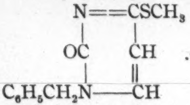
3-Methyluracil,  .—When the above mercaptopyrimidine was boiled with strong hydrochloric acid mercaptan was readily given off and on evaporating the acid under diminished pressure colorless prisms were obtained. The crude product melted at 223°–226° while 1-methyl uracil melts at 174°–175°.[1]

The material was very soluble in water and boiling alcohol. It crystallized from absolute alcohol in rectangular prisms and from hot saturated, aqueous solutions in needles which melted at 232° to an oil without effervescence. It gave no red color with diazobenzenesulphonic acid in presence of sodium hydroxide. With bromine water and barium hydroxide it gave a purple precipitate. 3-Methyluracil is less soluble in cold water than 1-methyluracil.

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	21.90

Some of the above material was dissolved in cold dilute sodium hydroxide and the solution carefully neutralized with dilute hydrochloric acid. The pyrimidine was recovered unaltered and melted at 232°.

2-Oxy-3-benzyl-6-methylmercaptopyrimidine,

 .—Two grams of 2-oxy-6-methylmercaptopyrimidine and 1.8 grams of benzyl chloride were dissolved in about 30 cc. of alcohol containing one molecular proportion of potassium hydroxide (0.8 gram). There was an immediate

---

[1] Johnson and Heyl: This Journal, **37**, 633 (1907).

reaction when the mixture was heated and potassium chloride separated. The solution was warmed on the steam bath until it gave no alkaline reaction. The potassium chloride was then filtered off and the solution was cooled, whereupon the benzyl derivative separated in prisms melting at 148°–149° to an oil without effervescence. This melting point was not raised by recrystallizing from alcohol. The alcohol filtrates were evaporated to dryness on the steam bath and the residue was treated with dilute sodium hydroxide to remove any unaltered material. The insoluble portion melted without further purification at 146°–148° and was practically pure 3-benzyl derivative. The yield of this pyrimidine was 2.9 grams, or 90 per cent of the calculated. No evidence of the formation of an isomeric benzyl derivative was obtained.

	Calculated for $C_{12}H_{12}ON_2S$.	Found.
N	12.06	12.19

When this mercaptobenzylpyrimidine was boiled with hydrochloric acid it gave a quantitative yield of 3-benzyluracil[1] melting at 172°–173°. A mixture of this compound and a sample of 3-benzyluracil melted at 172°–173°, while a mixture of the pyrimidine in question and 1-benzyluracil (m. p. 175°) melted at 140°–145°.

Action of Methyl Iodide on 2-Ethylmercapto-6-oxypyrimidine.—We have reexamined the action of methyl iodide on the potassium salt of 2-ethylmercapto-6-oxypyrimidine[2] and we now find that both 1- and 3-methyl derivatives are formed. In the previous work only the 1-methyl derivative was isolated. A mixture of 2-ethylmercapto-6-oxypyrimidine (15.2 grams), potassium hydroxide (5.6 grams), and methyl iodide (18 grams), in 75 cc. of alcohol was warmed on the steam bath until the solution gave a neutral reaction. It was then evaporated to a syrup and a little water was added. This caused the separation of 3.6 grams of 1-methyl-2-ethylmercapto-6-oxypyrimidine which was filtered off. The filtrate was boiled with hydrochloric acid and evaporated to dryness and the residue was repeatedly extracted with boiling alcohol. The part insoluble in alcohol proved to be uracil. The alcoholic solution was decolorized with animal charcoal and some sulphur dioxide. The alcohol was evaporated and the residue was fractionally crystallized from water. We then obtained the 3-methyluracil melting at 232° and the 1-methyl derivative melting at 174°. Owing to their similar solubility in alcohol, water, and other solvents it is impossible to make even an approximately quantitative separation by this treatment. It seems to us, however, that the 1-methyl derivative is formed in largest quantity. Further work may show that these proportions vary with change of conditions.

---

[1] Johnson and Derby: This Journal, **40**, 444 (1908).

[2] Johnson and Heyl: *Loc. cit.*

New Haven, Conn.,
April, 1909.

CONDUCTIVITY AND VISCOSITY IN MIXED SOLVENTS CONTAINING GLYCEROL.

By M. R. Schmidt and Harry C. Jones.

[ELEVENTH COMMUNICATION.]

Part I.

This investigation is the latest in a series which has been carried out in the Physical Chemical Laboratory of the Johns Hopkins University, dealing with the relations between electrical conductivity and viscosity of solutions of various electrolytes in certain nonaqueous solvents, and in mixtures of these solvents with water and with each other. The results of the first seven investigations have been published as Monograph No. 80, of the Carnegie Institution of Washington, 1907. Since that time an eighth communication by Jones and Veazey[1] has appeared, and a ninth, by Jones and Mahin,[2] is about to be published. It now seems desirable to bring together the more important facts thus far established and the conclusions drawn from them.

Previous Work in Nonaqueous Solvents.

The modern theory of solutions has been largely based on experimental work done in aqueous solutions, but lately an increasing amount of attention has been given to the behavior of solutions in solvents other than water; and the present work has to deal with certain questions that presented themselves in connection with solutions in methyl and ethyl alcohols, acetone, and mixtures of these solvents with water and with one another.

---

[1] Z. physik. Chem., **62**, 44 (1908).

[2] To appear in Z. physik. Chem., 1909, Jubelband zu Arrhenius.

Considerable work had already been done on solutions in these solvents, and a few measurements had been made of solutions in mixtures. Carrara[1] carried out an extensive investigation, using methyl alcohol as the solvent, and studying the electrical conductivity of a great variety of salts. Zelinsky and Krapiwin[2] also worked with solutions in methyl alcohol, and with a few in a mixture of methyl alcohol and water. This work will be referred to again.

Hartwig,[3] Vicentini,[4] Cattaneo,[5] and Völlmer[6] have determined the conductivity of a great variety of salts in ethyl alcohol. A few measurements have been made in some of the higher alcohols by Schlamp,[7] Carrara,[8] and Kablukoff.[9] Cattaneo[10] and Carrara[11] also published the results of a good deal of work in acetone. The work of Dutoit and Aston,[12] as well as that of Dutoit and Friderich,[13] should be mentioned here. Dutoit and Aston formulated the hypothesis that the dissociating power of a solvent is a direct function of its degree of association in the pure state. This relation has been found to hold for a large number of cases, but there are many and important exceptions to it, and its value has often been overestimated.

By far the largest and most important work on organic solvents is the series of investigations carried out by Walden and his students.

---

[1] Gazz. Chim. Ital., **26** [1], 119 (1896).
[2] Z. physik. Chem., **21**, 35 (1896).
[3] Wied. Ann., **33**, 58 (1888); **43**, 838 (1891).
[4] Beibl. Wied. Ann., **9**, 131 (1885).
[5] *Ibid.*, **18**, 219, 365 (1894).
[6] Wied. Ann., **52**, 328 (1894).
[7] Z. physik. Chem., **14**, 272 (1894).
[8] Gazz. Chim. Ital., **27** [1], 221 (1897).
[9] Z. physik. Chem., **4**, 432 (1889).
[10] Rend. R. Accad. Linc. [5], **4**, 2 sem., 63.
[11] *Loc. cit.*
[12] Compt. Rend., **125**, 240 (1897).
[13] Bull. Soc. Chim. [3], **19**, 321 (1897).

Ten papers[1] have appeared from his laboratory, dealing with the relations between conductivity and viscosity, dielectric constants, refractive indices, solvent power, etc., for about thirty organic solvents.

Mixed Solvents.

Wakeman[2] made an extensive investigation with aqueous ethyl alcohol, finding that the conductivity of organic acids in it decreased with increasing amounts of alcohol. Zelinsky and Krapiwin[3] obtained the interesting result that the conductivity of sodium and ammonium bromides and iodides in aqueous methyl alcohol containing 50 per cent alcohol is less than the conductivity in either the alcohol or the water. Wakeman found from his results that the equation

$$\frac{\Delta}{p(100 - p)} = \text{constant}$$

held satisfactorily for many substances in mixtures of ethyl alcohol and water, Δ being the difference between the conductivity of the electrolyte in water and in the mixture, and p the percentage of alcohol by volume.

Cohen[4] found the relation

$$\frac{\mu_v \, \text{H}_2\text{O}}{\mu_v \, \text{H}_2\text{O. Alc.}} = \text{constant}$$

to hold independently of temperature and concentration.

Conductivity and Viscosity.

Wiedemann[5] was the first to point out a connection between conductivity and viscosity. From his work on solutions of copper sulphate, he formulated a relation

$$\frac{ky}{p} = \text{constant},$$

---

[1] Z. physik. Chem., **46,** 103; **54,** 129; **55,** 207; **55,** 281, 683; **58,** 479; **59,** 192; **59,** 385; **60,** 87; **61,** 633.

[2] *Ibid.*, **11,** 49 (1893).

[3] *Loc. cit.*

[4] Z. physik. Chem., **25,** 31 (1898).

[5] Pogg. Ann., **99,** 229 (1856).

where k is the conductivity of a solution of concentration p, and y is its viscosity.

Stephan[1] showed that in alcohol and water mixtures the temperature coefficients of conductivity and fluidity were nearly the same. He also found a minimum conductivity in certain mixtures.

For a complete discussion of the electrochemistry of non-aqueous solutions, one should consult Carrara's "Elettrochimica delle soluzioni non aquose"[2] which covers the literature well up to the year 1906.

Experimental.

The work of Jones and his assistants comprises a uniform series of investigations, the same experimental methods being used in each. The conductivities were determined by the ordinary Kohlrausch method. The bridge wire, resistance boxes, thermometers, etc., were all calibrated or tested against the same standard instruments. Measurements were made at two temperatures, 0° and 25°.

The conductivity water was purified by the method of Jones and Mackay,[3] and had a mean conductivity at 0° of 1×10^{-6}, and twice that amount at 25°. The alcohols were purified by careful distillations after being boiled with lime several times. The conductivity of the ethyl alcohol was between 0.2×10^{-6} and 2×10^{-6}, and that of the methyl alcohol was about the same as that of the water. The acetone was dried by calcium chloride, and had an average conductivity of about 0.6×10^{-6}.

Viscosity measurements were made by means of the Ostwald viscometer.[4]

The work of Thorpe and Rodger[5] was consulted for the values of the viscosity of water at 0° and 25°.

The standard of conductivity is, in all cases, that of a fiftieth-normal solution of potassium chloride at 25°, which is taken as 129.7 reciprocal Siemens's units.

---

[1] Wied. Ann., **17**, 673 (1883).

[2] Gazz. Chim. Ital., **37** [1], 1 (1907); Ahrens' Sammlung, **12**, 11 (1908).

[3] THIS JOURNAL, **19**, 91 (1897).

[4] Phys.-chem. Mess., 2nd. Ed., p. 260.

[5] Phil. Trans., **185**, A, 307 (1894).

Jones and Lindsay undertook a further investigation of the phenomenon observed by Zelinsky and Krapiwin, and by Cohen, namely, a minimum value of conductivity in a fifty per cent mixture of methyl alcohol and water. The solvents used were methyl, ethyl, and *n*-propyl alcohols, water, and binary mixtures of these liquids. The electrolytes studied were potassium, cadmium, and strontium iodides, ammonium bromide, and lithium nitrate. In every case it was found that the molecular conductivity of solutions in the mixed solvents was less than the average calculated from the conductivities in the components. In some cases, curves with well-defined minima were obtained at 0°, some of which persisted at 25°, while others developed into sagging curves with no minima.

As a partial explanation of these facts, this tentative suggestion was made:

It is known that water and the alcohols are highly associated substances, that is, their molecules in the liquid state exist as complexes, the composition of which varies with the temperature. Now, according to the hypothesis of Dutoit and Aston, only those substances which are associated can dissociate molecules. Hence, water and the alcohols, on coming in contact, lower the state of association of each other, until a condition of equilibrium is reached. The mixture, being now less associated than its components, should have less dissociating power than the latter, and this is actually the case in every instance studied. Moreover, the lowering of conductivity is more marked when the alcohols are mixed with water than when they are mixed with each other, because they are associated to a less degree than water.

This conclusion was subsequently confirmed by Jones and Murray.[1] By means of cryoscopic measurements with water, formic and acetic acids, and mixtures of these liquids, they showed that the molecular weights of these substances were always less, even in very concentrated solutions, than the values obtained by Ramsay and Shields, who had found that these liquids are all highly associated in the pure condition.

---

[1] This Journal, **30**, 193 (1903).

Jones and Carroll[1] extended the work of Jones and Lindsay. The solvents used were water, methyl and ethyl alcohols, and various mixtures of these with one another. The electrolytes chosen were cadmium iodide, sodium iodide, calcium nitrate, hydrochloric acid, sodium acetate, and potassium iodide. Cadmium iodide in mixtures of methyl alcohol and water showed no minimum, except in the curves for $V = 16$, $V = 32$, and $V = 64$ at 0°. Here a minimum appeared in the 75 per cent mixture. In all cases, however, the conductivities were less than the average values. In mixtures of ethyl alcohol and water, the same salt showed entirely similar phenomena, though no minima were observed. Sodium iodide gave a well-defined minimum in the 50 per cent mixture of methyl alcohol and water. Calcium nitrate in the same solvents gave no minimum, while the conductivities again did not obey the law of averages. Hydrochloric acid gave irregular results, but a minimum was noticed in a mixture containing 90 per cent methyl alcohol. Sodium acetate in various mixtures of acetic acid and water gave entirely irregular figures.

An effort was made to determine the dissociating power of the methyl alcohol–water mixtures, since it had been noticed that the molecular conductivity, μ_v, for hydrochloric acid became constant at rather small dilutions in these solvents. Limiting values of conductivity were obtained for sodium, potassium, and ammonium iodides and bromides, and lithium nitrate, in 50 per cent methyl alcohol. In all these cases, the dissociation was complete in the mixture at a dilution considerably less than that necessary for complete dissociation in water or methyl alcohol. It now remained to find the cause of the minimum.

Two factors are to be considered, amount of dissociation, and ionic mobility. The first has been eliminated, hence the minimum must be caused by a decrease in ionic mobility. From the results of various observers, it was found that the viscosity of aqueous alcohol in the neighborhood of a 50 per cent mixture is higher than that of either of its constituents.

---

[1] This Journal, **32**, 521 (1904).

Furthermore, the change in viscosity with increasing content of alcohol is more marked at low temperatures than at higher, and rise in temperature shifts the maximum in viscosity, or minimum in fluidity, slightly towards the mixture containing the greater percentage of alcohol. These phenomena are closely paralleled by the conductivity minima. The latter all occur in or near the 50 per cent mixtures, and are more marked at 0° than at 25°. Cadmium iodide, for instance, shows a minimum at 0° in three solutions, but none at 25°. Potassium iodide, strontium iodide, and lithium nitrate give minima in the 50 per cent mixture at 0°, which move to the 75 per cent mixture at 25°.

A method was then devised for comparing the variations in fluidity and conductivity, and for studying the effect on conductivity of changes in fluidity. The differences between the (calculated) average values and the observed conductivities and fluidities in the various mixtures were expressed in percentages, and in all cases the variation in fluidity was found to be greater than the variation in conductivity. Letting $\Delta\phi$ and $\Delta\mu_v$ represent the two variations, then $\frac{\Delta\phi - \Delta\mu_v}{\Delta\phi}$ represents the relative effect of variation in fluidity on conductivity. If the two effects are equal, the expression becomes equal to zero. It was found that in the 40 per cent mixtures, the effect of change in fluidity on conductivity is greatest. Finally, the temperature coefficients of conductivity and of fluidity were not found to differ markedly; in other words, $\frac{\mu_v}{\phi}$ is nearly a constant.

Jones and Carroll therefore conclude that the decrease in conductivity in binary mixtures is due primarily to a decrease in the fluidity of the solvent, and, consequently, a decrease in the ionic mobility, and secondarily to the effect of one associated solvent on the association of another.

A quantitative study of the relation between the conductivity and viscosity of different solutions was then made. In order that data for different solvents might be comparable, measurements were made with "comparable equivalent solutions," that is, solutions containing the same number of gram-molecules of electrolyte in the same number of gram-molecules of solvents. The result was that the conductivities of such solutions were found to be inversely proportional to the viscosity of the solvent, and directly proportional to the association factor of the solvent, or to the amount of dissociation of the electrolyte in that solvent. Otherwise expressed,

$$\frac{\mu_v \eta}{x} = \text{constant or } \frac{\mu_v \eta}{\alpha} = \text{constant.}$$

The work of Bassett[1] showed that silver nitrate, in mixtures of methyl alcohol and ethyl alcohol with water, presented phenomena entirely in accord with the observations of Jones and Lindsay and of Jones and Carroll. The conductivity curves for ethyl alcohol-water solutions fall far below the straight line of averages, but give no minima; the methyl alcohol–water curves, on the other hand, give well-marked minima at both 0° and 25°, the variation from the average being more pronounced at the lower temperature.

Jones and Bingham[2] introduced another solvent into the investigation, namely, *acetone*. The electrolytes studied were lithium nitrate, potassium iodide, and calcium nitrate, and quite unexpected results were obtained. Lithium nitrate, in mixtures of acetone and water, gave curves with an inflection point at low dilutions and at 0°, which developed minima in the higher dilutions at 0°. The conductivity curves for solutions in mixtures of methyl and ethyl alcohols with acetone gave *maxima*, which, in the higher dilutions, occurred always in the mixtures containing 75 per cent acetone. The curves are very nearly straight lines below this point, but drop rapidly to the values *in 100 per cent* acetone. This fact is important in connection with the work of Mahin, to be considered later. Potassium iodide in mixtures of the alcohols with acetone gave conductivity curves which were very nearly straight lines, either slightly convex or concave towards the axis denoting percentages of acetone. In mixtures of acetone and water, the same salt gave pronounced minima in the neighborhood of the 50 per cent mixtures. Calcium nitrate in mixtures of methyl and ethyl alcohols with acetone gave curves with maxima at both 0° and 25°. In mixtures with water, the results were again irregular. In the first place, the values of μ_v for calcium nitrate in acetone are surprisingly small, less than those for lithium nitrate or potassium iodide, although it is a ternary electrolyte. In consequence, the curves for acetone–water mixtures, at dilutions greater than $V = 400$, reach a minimum in the 50 per cent mixture, and rise to the 75 per cent mixtures—in this point resembling the curves for potassium iodide—but thereafter sink to the small values on the ordinate representing 100 per cent acetone.

---

[1] This Journal, **32**, 409 (1904).
[2] *Ibid.*, **34**, 481 (1905).

The viscosity measurements brought to light the facts that the fluidity curves of mixtures of the alcohols with acetone are nearly straight lines, while the acetone–water mixtures give a minimum fluidity in the 50 per cent mixture. In general, therefore, the relation found by Jones and Carroll holds for mixtures containing acetone, that is, there exists a parallelism between the conductivity and fluidity curves. However, the maximum conductivity obtained with solutions of calcium and lithium nitrates in mixtures of acetone with the alcohols demands explanation. Two possible causes suggest themselves at once.

First, there may be an increase in dissociation in the 75 per cent mixtures, where the maximum occurs. Secondly, there may be an increased mobility of the ions, due to a diminution in the size of the ionic spheres. The idea of ionic spheres, proposed by Kohlrausch and by Jones, postulates the existence of an atmosphere of solvent molecules clustered about the ion. To decide between these two possibilities, we may first consider the increase in dissociation. The fluidity data show that the acetone-alcohol mixtures are not more associated than the pure solvents; hence, using Dutoit and Aston's hypothesis, we should not expect to find greater dissociation in the mixtures. Moreover, while it is true that the maximum conductivity occurs in the 75 per cent mixture, this is true only for dilute solutions, the maximum shifting to the 25 per cent mixture as the concentration increases. This would not occur if the 75 per cent mixture had the greatest dissociating power. Therefore, the tentative view is accepted, that the maximum in conductivity is due to a change in the dimensions of the ionic spheres, and a consequent increase in migration velocity.

The conclusion of Dutoit and Friderich, and of Jones and Carroll, that conductivity is proportional to dissociation and inversely proportional to viscosity, must be supplemented by taking into consideration the possible changes in the size of the ionic spheres of solvent molecules.

Jones and Rouiller[1] undertook the study of silver nitrate. This salt gave results practically identical with those obtained by Jones and Bingham for lithium and calcium nitrates. The conductivity curves for acetone-water mixtures gave inflection points in the higher concentrations, and a pseudo-maximum in the 75 per cent mixture, the value of the molecular conductivities declining rapidly, however, to the figures for pure acetone. The curves for mixtures of methyl and ethyl alcohols are nearly straight lines, following the fluidity curves; and maxima are found in the acetone-alcohol curves.

The investigation was extended by McMaster[2] in a study of lithium bromide and cobalt chloride. The former behaved normally in all the mixtures of the alcohols and water; that is to say, a minimum was noticed in the conductivity curves at 0° and 25° in mixtures of the alcohols with water, while the results for mixtures of the two alcohols obeyed the law of averages almost exactly. In mixtures containing acetone, relations were found very closely analogous to those obtained by Bingham in the case of lithium nitrate. The solutions in alcohol-acetone gave maxima of conductivity in the 75 per cent acetone mixture; while the solutions in water gave minima at the higher dilutions and inflection points at the lower dilutions. The unusual behavior of the acetone mixtures is here again very evident.

Cobalt chloride, on the other hand, gave unexpected results. In the first place, the conductivity of its solutions in ethyl alcohol is surprisingly low, being only about 15 per cent as great as in water. In ethyl alcohol-water mixtures, cobalt chloride gave an inflection point in nearly all the solutions, but in the curves for $V = 200$ to $V = 1600$, at 0°, the value of μ_v is greater in the 75 per cent than in the 50 per cent mixture, thereafter declining to the lower values in pure ethyl alcohol. Exactly the same phenomenon is shown by calcium nitrate in acetone-water solutions, where the curves rise from the 50 per cent to the 75 per cent mixture, and drop off rapidly in pure acetone. Rouiller found similar results for silver nitrate. In methyl alcohol-water solutions, cobalt chloride is normal, giving pronounced minima in the 50 or 75 per cent mixtures. Methyl alcohol-ethyl alcohol solutions gave nearly straight lines, as did also solutions in acetone-methyl alcohol. In the last cases the fluidity curves are also nearly straight lines, but the acetone-methyl alcohol conductivity curves have a slope which is the reverse of the fluidity curve. Acetone and ethyl alcohol gave a maximum in the 25 per cent mixture.

---

[1] THIS JOURNAL, **36**, 427 (1906).

[2] *Ibid.*, **36**, 325 (1906).

In most of the above cases, we see that the conductivity varies directly as the fluidity, and fluidity minima are usually accompanied by conductivity minima. The converse, that conductivity minima were accompanied by fluidity minima, was not always found to be true, as, for instance, with cobalt chloride in acetone-ethyl alcohol. Here a maximum of conductivity is found in mixtures giving a fluidity curve which differs by less than experimental error from a straight line. Again, the conductivity curves for acetone-water show inflection points, while the fluidity curve has a minimum. These apparently irregular results are to be considered again in the work of Jones and Mahin.

In explanation of the minimum of conductivity, Jones and McMaster adopt the view that the diminution in the fluidity of the solvent is an important factor in determining the conductivity minimum. But this does not account entirely for the phenomenon. The change in the size of the ionic sphere, the atmosphere surrounding the ion, must also be considered. The velocity of the ion depends not only on its composition, but also on its attraction for the solvent.

There yet remain for consideration the several maxima of conductivity noticed in this work as well as in that of Bingham. The discussion of the latter work has shown that it is improbable that the maxima are due to an increase in dissociating power in the mixture where they occur. Moreover, an examination of the conductivities of lithium bromide and cobalt chloride shows that complete dissociation is more nearly reached in the pure solvents than in the mixtures where the maxima are found. Hence, it was concluded that the cause of the effect is primarily a change in the dimensions of the ionic spheres.

Some points of interest were noted in connection with the temperature coefficients of conductivity and of fluidity. First, in nearly every case the temperature coefficients of conductivity are greater in the more dilute than in the more concentrated solutions. The work of Jones has shown that in practically all solutions there is some combination between solvent and solute, and that the solvates become more complex as the dilution increases. Therefore, change in temperature, which affects the complex solvates most, has a greater effect on the conductivity of the more dilute solutions.

A second point worth noting was that in certain solutions negative temperature coefficients of conductivity were found. These manifested themselves in solutions of cobalt chloride in acetone, in 75 per cent acetone and methyl alcohol, and in 50 and 75 per cent acetone and ethyl alcohol. In the 75 per cent acetone and methyl alcohol, when $V = 200$, the temperature coefficient is *zero*.

The change in conductivity with temperature is the algebraic sum of two opposing influences. First, rise in temperature diminishes dissociation; secondly, rise in temperature is accompanied by an increase in fluidity. The first of the processes tends to decrease conductivity, the second to increase it. When the sum is positive, we have increasing conductivity with rise in temperature, as is usually found to be the case. In the one instance mentioned above, the two forces are equal, and the conductivity is independent of the temperature.

The investigation of Jones and Veazey[1] included a study of the behavior of copper chloride and potassium sulphocyanate. Both of these electrolytes gave results which were almost entirely "normal;" that is, conductivity curves followed fluidity curves in every case except two. These exceptions were the curves for copper chloride in mixtures of the alcohols with water. No minima were found here corresponding to the well-marked minimum in fluidity, although the conductivities were always less than required by the law of averages. An inflection point occurs between the 50 and 75 per cent mixtures. The conductivity curves of potassium sulphocyanate show no such irregularity, but are in every respect parallel to the fluidity curves of the solvents.

In addition to determining the fluidities of the various solvent mixtures, Jones and Veazey measured the fluidities of solutions of potassium sulphocyanate in these mixtures. It was found that in many cases the fluidity of the solution is greater than the fluidity of the solvent; in other words, potassium sulphocyanate, under certain conditions, has a negative viscosity coefficient. In mixtures of methyl alcohol and water, the viscosity of the tenth-normal solutions is less than that of the 0, 25, and 50 per cent solvent mixtures, and greater than the 75 per cent mixture, becoming equal at some point corresponding to about 65 per cent alcohol. The same phenomena repeat themselves in ethyl alcohol-water mixtures. With acetone and water, the negative viscosity coefficient again becomes apparent, this time only in the 0 and 25 per cent mixtures. In the other mixed solvents, the viscosity is increased by the addition of the solute.

An examination of the literature relating to viscosity brought to light the important fact that, in general, only salts of potassium, rubidium, and caesium are known to lower the viscosity of water. Very few other cases of negative viscosity have been found, and not all salts of these metals behave alike in this respect. For instance, the sulphate, ferrocyanide, ferricyanide, and chromate of potassium give positive viscosity coefficients. And it is not remarkable that in the presence of certain anions, the alkali cations do not give negative viscosity coefficients. Viscosity must be considered to be a property which is a function of the nature of all the particles in a solution, and it is perfectly clear that here, as in conductivity, two opposing influences may be operative, the potassium cation, for instance, tending to lower the viscosity and the anion tending to increase it. If the algebraic sum is positive, a positive viscosity results, and *vice versa*, the actual viscosity of the solution being dependent on the relative action of the two ions.

---

[1] THIS JOURNAL, **37**, 405 (1907); Z. physik. Chem., **61**, 641 (1908).

The facts have been presented showing that in aqueous solution, or in solutions containing as much as 50 per cent of water, potassium sulphocyanate produces a lowering of the viscosity. What is the mechanism of this effect?

The work of Thorpe and Rodger has shown that viscosity phenomena are, in all probability, dependent upon the frictional surfaces of the various particles in any solution. If the total frictional surface can be diminished by any means, other factors remaining constant, the viscosity will be lowered. We may actually realize this by bringing into a solvent a substance which has a large molecular volume, or which gives ions having large ionic volumes. The total frictional surface proportional to the mass is thus lessened, since the surface increases as the square of the diameter of the particles, while the mass increases as the cube. Potassium, rubidium, and caesium salts, as we have said, lower the viscosity of water. Are their atomic volumes, accordingly, larger than those of other elements? The periodic curve of atomic volumes answers this question at once. The alkali metals occupy the maxima of the curve, and no other metals have atomic volumes to be compared with them. Moreover, that element having the greatest atomic volume—caesium—should have the greatest negative viscosity coefficient. This point is soon tested by reference to the work of Wagner.[1] If the viscosity of water is taken as unity, a normal solution of caesium chloride lowers it to 0.9775, a normal solution of rubidium chloride gives 0.9846, and potassium chloride 0.9872. Thus the effect on viscosity varies directly as the atomic volume of the cation, caesium having an atomic volume of 74, rubidium of 57, and potassium 47.

---

[1] Z. physik. Chem., **5**, 35 (1890).

It will be remembered that minima of fluidity were found in mixtures of water with the alcohols or with acetone, accompanied usually by minima in conductivity. The fact also came out that in those mixtures which have the minimum fluidity, the temperature coefficients of conductivity are largest. The explanation of this is sufficiently evident. Each solvent, highly associated in the pure condition, breaks down the association of the other, as shown by Jones and Murray, so that the resulting mixture is composed of a greater number of smaller molecules in a given volume. Simple molecules would probably have greater chemical activity than the more complex ones and would combine with the solute to a greater extent. The effect of heat on such solvates would be greater with increasing complexity of the solvate. In connection with this breaking down of the solvents into simpler aggregates, the total internal frictional surface would be increased, and an increase in viscosity is the result. Again, in terms of Dutoit and Aston's hypothesis, the dissociating power of such a mixture should be less than that of the pure solvents, and this is an important factor in determining the conductivity minimum, as pointed out by Jones and Bingham. It is noticed that in these mixtures of minimum fluidity, there is a smaller increase of conductivity with dilution than in the other mixtures, and this is, of course, a consequence of the view here adopted.

In a second communication,[1] Jones and Veazey took up a study of solutions of tetraethylammonium iodide—Walden's "Normalelektrolyt"—in mixtures of water, the alcohols, and nitrobenzene. The latter is a solvent of a type entirely different from the hydroxy compounds or acetone, and it was important to know whether the relations previously found would hold for mixtures containing this substance.

---

[1] Z. physik. Chem., **62**, 41 (1908).

In mixtures of both the alcohols with water, tetraethylammonium iodide shows a well-defined conductivity minimum in the neighborhood of the 50 or 75 per cent mixtures at both 0° and 25°. In mixtures of the alcohols with each other, no minima appeared, although the values are less than the averages. Mixtures of methyl alcohol and nitrobenzene behaved similarly, but mixtures of ethyl alcohol and nitrobenzene gave a maximum in the solutions containing 25 per cent of the latter. The fluidity curves of mixtures of water and the alcohols have already been sufficiently treated, and here, as before, the conductivity curves follow them closely. The same general relations appear in mixtures of nitrobenzene and the alcohols. A fluidity maximum shows itself in mixtures containing 25 per cent of nitrobenzene, with either alcohol, and at 0° and 25°. Hence, the conductivity curves, in the case of nitrobenzene-ethyl alcohol mixtures at least, follow the fluidity curves, and the variation with nitrobenzene-methyl alcohol is slight.

It has now been shown that for all the solvents worked with, it is practically a constant phenomenon for conductivity curves to have the same general characteristics as fluidity curves. On the other hand, we must not lose sight of the fact that several well-marked exceptions have been found, and notably in mixtures containing acetone. Here the fluidity curves for water-acetone have minima, and for acetone-alcohol are nearly straight lines, while the conductivity curves for lithium bromide, lithium nitrate, cobalt chloride, and calcium nitrate show pronounced maxima, or pseudomaxima. Moreover, the values of the molecular conductivities in acetone are abnormally low, except for lithium salts.

In the work of Walden,[1] already referred to, it was found that the product of the limiting molecular conductivity of tetraethylammonium iodide and the viscosity of its infinitely dilute solutions is nearly a constant for about thirty organic solvents, and equal to about 0.7. Water and glycol are exceptions, giving products equal to 1.0 and 1.32, respectively. The product $\mu_\infty \eta$ is also independent of temperature. Therefore, generally speaking, conductivity varies as the fluidity of the solvent. But, as we have shown, in certain solutions containing acetone, this relation no longer holds.

---

[1] Z. physik. Chem., 55, 207 (1906).

It may further be noted that Jones has shown[1] that cadmium iodide and ammonium sulphocyanate, in acetone solutions, have abnormally high molecular weights, although such solutions conduct the current. He pointed out that these facts indicate simultaneous association and dissociation of the solute; a high concentration of molecular complexes, which causes an abnormal apparent molecular weight, coexisting with a low ionic concentration, which causes a low conductivity value. A consideration of these points suggested to Jones and Mahin several lines of inquiry, which were taken up in the ninth communication.[2] They sought to answer the following questions:

1. Will those salts that have, at ordinary concentration, abnormally low values for molecular conductivity possess, when completely dissociated, values which are inversely proportional to the coefficient of viscosity?

2. If so, is the product of molecular conductivity and viscosity constant for mixed solvents and at different temperatures?

3. Is the value of the constant the same for different electrolytes?

4. Are the abnormal conductivities in acetone and mixtures of acetone with other solvents due to association of the salt?

The first salt studied was lithium nitrate. Extreme precautions were taken to insure purity of the solvents, and measurements were carried to dilutions as high as 200,000 liters wherever practicable. Under these conditions, the conductivity curves assumed forms which differed markedly from those obtained for dilutions between 10 and 1600 liters, and which closely resembled the fluidity curves. Moreover, the product of the viscosity coefficient and the maximum conductivity in solutions of acetone mixed with the alcohols has a mean value of 0.62, agreeing well with Walden's value of 0.70 for simple solvents, and being independent of temperature. With acetone-water mixtures, the product varies between 1.00, the value for water, and 0.63, the value for acetone.

---

[1] This Journal, **27**, 16 (1902).

[2] To appear in Z. physik. Chem., August, 1909.

Some determinations of the molecular weight of lithium nitrate in acetone by the boiling point method brought out interesting results. The concentration of the solutions varied roughly between normal and tenth-normal. Even in the more dilute solutions, the indicated molecular weight was 83.1, while the value required by the formula $LiNO_3$ is 69.07. This accounts for the low conductivity of lithium nitrate in acetone solutions of not very great dilution.

As already stated, cadmium iodide was found by Jones to be associated in acetone, and a study of this salt was next made. Results in this case were not so satisfactory as with lithium nitrate. The conductivity curves show signs of regaining a similarity to the fluidity curves, but the resemblance is not so close as with the other salt. Moreover, the product of the viscosity by the maximum conductivity is irregular. The conductivity data show that in most cases a limiting value was not reached with cadmium iodide, and some solutions more nearly approached the true values than others, thus causing the fluctuations in the value of the product. It must be borne in mind that conductivity measurements at dilutions so great (400,000 liters) that the correction for the conductivity of the solvent often amounts to more than 50 per cent of the total, are being made at a point where the method is taxed rather beyond its limitations; and it is not surprising that even with the utmost precautions, concordant results are not obtained. The failure of cadmium iodide to follow the behavior of lithium nitrate in very dilute solutions is merely negative evidence, and must be weighed as such.

Some boiling point determinations of cadmium iodide in acetone were made, and here too, considerable polymerization was found. In a 0.09 normal solution, the indicated molecular weight was 448, calculated 364.

Thus, the apparent exceptions to the relations found by Jones and his coworkers are seen to vanish when we are dealing with what are practically infinitely dilute solutions. The investigations have dealt with twelve electrolytes and six solvents, and in every instance the same relations are found to hold, connecting the molecular conductivity with the fluidity.

Jones and Mahin[1] also made a study of the conductivity and viscosity of lithium nitrate in ternary mixtures of the four solvents used above. The results were about what would be expected from a knowledge of the solutions in binary mixtures. The conductivity curves, in the great majority of cases, followed the fluidity curves, and no new relations were brought to light.

As a result of this work, we may make the general statement: If we mix methyl and ethyl alcohols, or methyl alcohol and acetone, the conductivity curves are very close to straight lines, and the fluidities of the mixture are nearly additive. Take, for instance, the last case mentioned. The table shows the fluidities of various mixtures of methyl alcohol with acetone at 0°, as determined by the viscometer, and also as calculated from those of the two components.

Fluidity of Mixtures of Methyl Alcohol and Acetone at 0°.

Per cent acetone	0	25	50	75	100
Fluidity observed	122.2	153.9	187.4	222.2	244.1
Fluidity calc.	...	152.7	183.2	213.7	...

The observed fluidities are very nearly the averages corresponding to the different mixtures. On the other hand, if we mix water with the alcohols, or with acetone, there is interaction between the components of the mixture, and certain of its physical properties are found no longer to bear simple relations to the properties of the single solvents. Otherwise expressed, the law of averages is not followed, and the properties of the mixture are not additive. Hence, we may conclude that water, mixed with the other three solvents, causes some deep-seated change in the state of molecular aggregation of the liquid molecules, while mixing the three organic solvents with each other causes no such change. The various mixed solvents may therefore be divided into two classes, those not containing water, with properties nearly or quite additive, and those containing water, with properties that are not the averages of the two components.

---

[1] This Journal, **41**, 433 (1909).

PART II.

It is thus seen that certain definite relations exist between the conductivity of various electrolytes dissolved in binary mixtures of four solvents, and the viscosity of their solutions. It was of interest to know whether similar relations would hold when one of the component solvents had a viscosity much greater than that of the other; in other words, whether the effect of one solvent on another follows the same laws, no matter what substances are used. The solvent eminently suited for this purpose is glycerol. Not only is its viscosity enormously greater than that of any other homogeneous liquid at ordinary temperatures, but several of its physical constants would lead us to expect glycerol to be well adapted as a solvent in making conductivity measurements. The dielectric constants and association factors of the solvents used in the previous work are given in Table I. The dielectric constants are taken from the work of Drude[1] and were all determined in the neighborhood of 18°, and the association factors are taken from the work of Ramsay and Shields,[2] and refer to nearly the same temperature.

Table I.

Solvent.	Dielectric constant.	Association factor.
Water	81.7	4.00
Methyl alcohol	32.5	3.43
Ethyl alcohol	21.7	2.74
Acetone	20.7	1.26

Glycerol has a dielectric constant of 16.5 at 18°, and hence, in terms of the Thomson–Nernst rule, should have a fairly high dissociating power. Moreover, if we assume Dutoit and Aston's hypothesis to hold even approximately for glycerol, the association factor of the latter, 1.80 at 20°, would lead to the same conclusion. The conductivity data will show that these expectations are well founded, and that glycerol is, in all probability, a solvent with a dissociating power rather above the average.

---

[1] Wied. Ann., **60**, 500.

[2] Z. physik. Chem., **12**, 433 (1893).

Glycerol as a Solvent.

It has, of course, been known for a long time that glycerol has remarkable solvent properties. Not only will it dissolve all deliquescent salts, such as many compounds of lithium and calcium, but it also takes up large quantities of nearly all the halogen salts of the common metals, including even those which are difficultly soluble in water, as well as many sulphates, nitrates, etc. In addition, the alcohol groups of glycerol react with metallic oxides and hydroxides, forming glycerates by a process analogous to the solution of sodium or potassium hydroxides in alcohol.

In spite of the ease with which very pure glycerol can be obtained in large quantity, very little work has been done with solutions in it. In various branches of manufacture, and especially in pharmacy, it has long had extensive use as a solvent, but no systematic study has been made of the properties of its solutions.

Cattaneo[1] measured the conductivity of a number of halogen salts of the metals in glycerol, and found that the conductivities are smaller than the corresponding values in water or alcohol, but greater than those in ether. He also states that the molecular conductivity increases only in the case of chlorides. This last statement is not at all confirmed by the present work.

Schöttner[2] carried out an extensive investigation on the viscosity of glycerol and of some of its mixtures with water. Arrhenius[3] measured the viscosity of certain organic substances, including glycerol, in aqueous solution, and found that the decrease of η with rising temperature is greatest when η is large. Schall and van Rijn[1] determined the relative times of flow of various mixtures of glycerol with small quantities of water and alcohol.

---

[1] Rend. Accad. Linc. [5], **2**, II, 112 (1893).

[2] Wien. Ber., **77**, 2, 682 (1878).

[3] Z. physik. Chem., **1**, 289 (1887).

EXPERIMENTAL.

Conductivity Apparatus.

The conductivity measurements were made by the Kohlrausch method, using a wire bridge and telephone receiver. The bridge wire was calibrated and found to be of uniform resistance throughout. The conductivity cells were of the form used by Jones and Bingham and subsequent workers in this laboratory. For use with the solutions in pure glycerol, two cells of a different type were used. The electrodes in one cell consisted of two concentric platinum cylinders, about 7 cm. long, and 18 and 22 mm. in diameter. They were maintained at a constant distance apart of about 2 mm. by means of several drops of fusion glass attached to the edges of the cylinders. The constant was very low, about 4.30. The other cell had as electrodes three cylinders, the outer and inner being joined by a thick branching platinum wire, and forming one electrode, while the middle cylinder formed the other. Drops of fusion glass also served here to keep the electrodes at a constant distance apart of about 1.5 mm. The cell constant was about 2.35. The electrodes of both cells were used without being covered with platinum black, and it was possible to obtain very sharp minima on the bridge with them. For instance, when the cell contained conductivity water, and a resistance of one or two thousand ohms was introduced into the circuit, the bridge could easily be read at points two mm. on each side of the true minimum. This form of cell has proved itself to be especially adapted to work with very viscous solutions. The large electrode surface permits of the cylinders being several mm. apart, without making the "capacity" of the cell too great; and this feature alone is of great advantage, as it allows very thick liquids to fill all the space between the electrodes, without the danger of imprisoning air bubbles. The escape of the latter is further facilitated by the vertical position of the cell walls. The "constants" of both cells showed only extremely slight variation throughout the work.

---

[1] Z. physik. Chem., **23**, 329 (1897).

The conductivity measurements are expressed in reciprocal Siemens's units, and the cell constants were determined by means of a fiftieth-normal potassium chloride solution, the molecular conductivity of which was taken as 129.7 at 25°.

Measurements were made at 25° and 35°. Glycerol, when maintained at 0° for a long period, undergoes a gradual change, resulting sometimes in the deposition of crystals. On this account, and for the reason that at low temperatures the substance is so extremely immobile that viscosity determinations are almost impossible, no measurements were made at 0°, as has been the custom in these investigations. The temperature coefficients of conductivity and viscosity are therefore not strictly comparable with those obtained by other workers for the same solutions between 0° and 25°.

The constant-temperature baths were of the form described before, and were maintained constant within 0°.03 of the desired temperatures. The thermometers were compared with a certificated Reichsanstalt instrument. The measuring flasks were calibrated to hold aliquot parts of the true liter at 20°, and solutions were brought to within 0°.2 of this temperature before filling to the mark.

Solvents.

Glycerol.—The glycerol used was Kahlbaum's "Glycerin, 1.26." Two determinations of different lots gave the same density, $D_{25}^{25} = 1.2586$. The specific conductivity varied from 0.5×10^{-7} to 0.7×10^{-7} at 25°. Some of the glycerol was distilled under diminished pressure, boiling at 160° under a pressure of 6 mm. The specific conductivity was not changed by this process, and the remainder of the glycerol was used without further treatment.

Water.—The water was purified essentially by the method of Jones and Mackay,[1] with a slight modification. The practice heretofore has been to distil ordinary distilled water from acidified potassium dichromate to destroy organic matter and retain ammonia, and then to redistil from a weaker chromic acid solution, forcing the steam from the second distillation through a solution of barium hydroxide. There can be no doubt that water prepared in this way still contains large quantities of carbon dioxide. The extreme rapidity with which the current of steam passes through the alkaline solution makes it impossible for the latter to come in contact with all of the vapor, and some of the carbon dioxide escapes with the steam to be condensed, giving water with a conductivity which has generally been about 2×10^{-6} at 25°. If, however, the second distillation is made from a solution containing barium hydroxide instead of acidified dichromate, the conductivity of the water is lowered considerably. Nearly all of the carbon dioxide is retained, and the conductivity of the water thus purified has rarely risen over 1.5×10^{-6}, and was many times as low as 1.2. In addition, the alkaline solution, probably owing to the presence of the fine crystals of barium carbonate, boils more quietly than the acid solution, with entire absence of bumping, and with consumption of much less gas.

---

[1] This Journal, **17**, 83 (1895).

Ethyl and Methyl Alcohols.—These were purified by boiling the commercial articles with fresh lime for a day, and then distilling again from more lime without transferring the alcohol in the air. A third distillation from lime was made if the specific gravity of the second distillate showed the presence of any appreciable quantity of water. Several more distillations were then made through a block-tin condenser. The conductivity of the ethyl alcohol ranged between 1.2×10^{-7} and 1.8×10^{-7}, although in one case it was as low as 0.9×10^{-7}. The value for the methyl alcohol was about 1.5×10^{-6} at 25°.

Work with mixtures containing acetone, which it was hoped would yield some interesting results, had to be given up, since glycerol and acetone are only slightly miscible.

The mixed solvents are made up on a volume basis, and in every case throughout the work, unless otherwise specified, "*n* per cent A and B" means *n* cc. of solvent A diluted to 100 cc. with solvent B.

Solutions.

All solutions were made on a volume-normal basis, at 20°, by direct weighing of the anhydrous salts. A tenth-normal mother solution was first made, from which the fiftieth and hundredth-normal solutions were prepared by dilution. The hundredth-normal solution then served as a mother solution for the two-, four-, and eight-hundredth-normal solutions, and from the last named the sixteen-hundredth-normal was prepared. The dilutions were made by means of calibrated flasks and burettes. It was found that if a little time was given, the solutions containing 25 and 50 per cent of glycerol would drain as completely as aqueous solutions, and the same calibration was used for all three. With the 75 per cent solutions, and especially with those in pure glycerol, the draining was incomplete, even though the burette stood two days. Accordingly, a different calibration was made for each of the three mixed solvents containing 75 per cent of glycerol, and for the pure glycerol itself. The amount to be delivered was run at a fixed rate of flow into a weighing glass, and its weight divided by the density of the solvent at 20°. The difference between the volume thus found and the volume read off was the amount clinging to the walls of the burette, and this quantity, which was about 0.60 cc. for 25 cc. of glycerol, was added with each measurement of the solutions. It was of course necessary to run the solutions out between the same two points on the burette each time, as otherwise the mean hydrostatic pressure would vary, causing corresponding variations in the rate of flow, with a marked effect on the amount which did not drain out. This precaution is important, as shown by the fact that a volume of glycerol drawn off between 0 and 25 on the burette lacked 0.65 cc. of 25 cc., while the same apparent volume, taken between 24 and 49, was 0.35 cc. less than the amount desired. The water calibration showed that this difference was not due to a great irregularity in the diameter of the burette. Another point which must be noted is the necessity of keeping the temperature of the working room very constant while measuring glycerol. The changes in volume of the glycerol are inconsiderable compared with the great changes in fluidity, and a calibration made for 20° would, by reason of the much greater fluidity of glycerol at a higher temperature, be very inaccurate at 22°.

In view of the fact that so little work has been done with solutions in glycerol, a few details of a practical nature may not be out of place. In spite of the great solvent power of glycerol, the actual rate of solution is very slow, and most substances can be dissolved only after a great deal of shaking and heating. It was customary in this work to heat the glycerol to almost 100° before adding it to the salt in the measuring flask. At this temperature, glycerol is quite fluid, and its solvent action is greatly enhanced. Nevertheless, it required, with lithium bromide and cobalt chloride, nearly three hours of practically continuous shaking, with the temperature at about 80°–100°, to effect the complete solution of one or two grams of the salts in 100 cc. of glycerol. Potassium iodide, on the other hand, dissolved as soon as the glycerol was warmed slightly, and gave a clear solution in less than five minutes. In view of the close relation of glycerol to the alcohols, and of the very slight solubility of potassium iodide in absolute alcohol, this behavior is surprising.

Much annoyance is caused by the ease with which glycerol imprisons air bubbles, which may require hours to rise. Especially is this likely to occur when the substance is poured into a burette. This difficulty may be obviated, however, by pouring the solutions in while hot, in which case the air bubbles will rise fairly rapidly; or by pouring the solutions in such a manner that the descending stream does not strike the walls of the burette except at the highest point to which the burette is to be filled. Thus manipulated, the glycerol flows down the burette walls without enclosing any air, and moreover, no time is lost in waiting for the upper part of the burette to drain before taking the initial reading.

Viscosity.

The determinations of viscosity were made by means of several Ostwald viscometers,[1] or this form as modified by Jones and Veazey.[2] For the solutions in pure glycerol, as well as for the solutions containing 75 per cent of glycerol, viscometers of very large bore were necessary. Two of these, made for us by Eimer and Amend, were very satisfactory. The small bulb had a capacity of about 4 cc., and the larger of about 30 cc. The "capillaries," having internal diameters of 1.1 and 2 mm., respectively, were 12 cm. long. As the time of flow of water through these viscometers was less than ten seconds, it was of course necessary to calibrate them by using a more viscous liquid, the viscosity of which was known. For this purpose, the viscosities of several solutions, containing about 50 per cent of glycerol, were determined in the smaller instruments, and then the times of flow of these liquids through the large viscometers were noted. A fixed amount of solution was introduced into the viscometer from a pipette, and after being raised to the upper mark by air pressure, was allowed to run through the capillary by its own weight. The times of flow were read with an accurate stopwatch. The viscosities were calculated from the formula

$$\frac{\eta}{\eta_0} = \frac{st}{s_0 t_0},$$

where η_0, s_0, and t_0 are the viscosity, density, and time of flow, respectively, of pure water, and η, s, and t the corresponding values for the liquid in question. The values of η_0 at 25° and 35° are taken from Thorpe and Rodger's work[3] on viscosity, being 0.00891 at 25° and 0.00720 at 35°. Fluidity, expressed by ϕ, is equal to $\frac{1}{\eta}$, and the temperature coefficients of fluidity are calculated from the formula

$$\text{temp. coef. } \phi = \frac{1}{\phi 25} \cdot \frac{\phi 35 - \phi 25}{10}.$$

The densities of the solutions were determined in pycnometers of the form described by Jones and Veazey.[2]

---

[1] Phys.-chem. Mess., 2nd Ed., p. 260.

[2] Z. physik. Chem., **61**, 651 (1908).

[3] Phil. Trans., **185**, A, 307 (1894).

The measurement of viscosity, for some reason, seems to be beset with much greater experimental error than would be expected, considering the simple nature of the operation. The values given in Landolt–Boernstein's "Tabellen" often show differences of more than one per cent in the results of various observers. During the present work, it was found to be almost impossible to get results that would agree even fairly well in duplicate determinations. It may at first sight be supposed that by using three "steps" to determine the viscosities of the thicker solutions, as was done in this work, experimental error is introduced at each step, so that the values found by means of instruments with wide capillaries would necessarily be of doubtful accuracy. As a mattter of fact, though experimental error is introduced, the departure of the values found from the true values is influenced much less by this fact than by an inherent difficulty in the method.

The Poisseuille formula for determining viscosity is $v = \frac{\pi r^4 pt}{8l\eta}$, where v is the volume of liquid, whose viscosity coefficient is η, which, under a pressure p, will flow in the time t through tube of length l and radius r. In deriving this formula, the liquid is considered as leaving the tube with a kinetic energy of zero, which, manifestly is an impossible condition in practice. If the liquid flows out of the tube with a positive kinetic energy, a correction must be introduced. On rearranging the formula, with the correction, it becomes

$$\eta = \frac{\pi r^4 pt}{8vl} - \frac{vd}{8\pi tl},$$

where d is the density of the liquid. In determining viscosities by the relative method—that is, by means of the Ostwald viscometer—the corrected formula is rarely used. For two liquids flowing by their own weight through the same instrument, between the same differences in level,

$$\frac{\eta_1}{\eta_2} = \frac{p_1 t_1}{p_2 t_2}.$$

But

$$\frac{p_1}{p_2} = \frac{\rho_1 gh}{\rho_2 gh} = \frac{\rho_1}{\rho_2},$$

whence $\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$, which is the ordinary formula.

It is evident from the corrected formula that when t is smallest, the correction is greatest. Hence, a greater error is introduced by measuring the viscosity of a liquid whose time of flow is much greater than that of the standard, than in the case of one with nearly the same viscosity as the standard. In other words, the error would be a minimum if t could be kept constant. Therefore, the error is kept lowest by using in each instrument liquids whose times of flow do not differ too greatly from t_0. As the correction is always negative, the viscosity of a liquid determined without using intermediate steps should be greater than if several viscometers are used. This is illustrated in the case of 75 per cent glycerol and methyl alcohol at 25°. T is the time of flow.

Table II.

Viscometer.	*T.* Water.	*T.* 50 per cent glycerol and methyl alcohol.	*T.* 50 per cent glycerol and water.	*T.* 75 per cent glycerol and methyl alcohol.	η.
A	74.4	749.0	450.0	4465.0	0.61735
1	..	74.7	45.7	445.6	0.6073
2	..	...	...	141.7	0.6073

Here η is calculated by the following methods:

For viscometer A. $\eta = \frac{0.00891 \times 4465 \times 1.1546}{1 \times 74.4} = 0.61735$ (1.1546 is the density of 75 per cent glycerol and methyl alcohol).

For viscometer 1. The viscosities of 50 per cent glycerol and water, and 50 per cent glycerol and methyl alcohol, were determined in A; then from the times of flow of these solutions through 1, two values were obtained which were used to determine viscosities in 1, and the mean value of η for 75 per cent glycerol and methyl alcohol is determined from them, using $T = 445.6$. The same process is employed for viscometer

2. It is seen that η determined by direct comparison with water is greater, as it should be, than η determined by using liquids of intermediate viscosities in several instruments.

Lithium Bromide.

The lithium bromide gave a flame test which showed no appreciable impurity. It was dried to constant weight at 150°, and was again dried after each exposure to the air. Table III. gives the molecular conductivities of lithium bromide in pure glycerol at 25°, 35°, and 45°. It will be noticed that while the values of μ_v are very small, yet they show a regular increase with dilution, as is the case with all liquids having a marked dissociating power.

Table III.—Conductivity of Lithium Bromide in Glycerol at 25°, 35°, and 45°.

V.	μ_v25°.	μ_v35°.	μ_v45°.	Temperature coefficients. 25°–35°.	Temperature coefficients. 35°–45°.
10	0.236	0.485	0.907	0.106	0.0871
50	0.260	0.540	1.010	0.107	0.0881
100	0.270	0.555	1.041	0.106	0.0875
200	0.272	0.565	1.050	0.106	0.0868
400	0.275	0.572	1.070	0.108	0.0871
800	0.280	0.579	1.085	0.107	0.0874
1600	0.287	0.593	1.109	0.107	0.0871

Table IV.—Conductivity of Lithium Bromide in Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	91.8	110.7	0.0205
50	101.1	121.9	0.0206
100	103.0	124.4	0.0208
200	105.2	127.4	0.0219
400	107.2	130.1	0.0213
800	114.4	136.1	0.0222
1600	114.6	137.5	0.0200

Table V.—Conductivity of Lithium Bromide in a Mixture of 25 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	45.6	57.4	0.0257
50	49.6	62.5	0.0261
100	50.8	64.0	0.0260
200	52.8	66.7	0.0264
400	52.2	65.5	0.0255
800	54.0	69.4	0.0285
1600	54.9	71.5	0.0300

Table VI.—Conductivity of Lithium Bromide in a Mixture of 50 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	17.3	23.4	0.0351
50	18.8	25.4	0.0348
100	19.1	25.7	0.0346
200	19.5	26.3	0.0350
400	20.0	27.0	0.0351
800	21.4	28.9	0.0352
1600	21.7	29.5	0.0361

Table VII.—Conductivity of Lithium Bromide in a Mixture of 75 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	3.84	5.96	0.0552
50	4.23	6.56	0.0552
100	4.27	6.63	0.0551
200	4.43	6.89	0.0557
400	4.51	6.99	0.0552
800	4.40	6.89	0.0566
1600	4.47	6.99	0.0567

Table VIII.—Conductivity of Lithium Bromide in Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	15.8	18.4	0.0162
50	23.0	26.7	0.0161
100	25.9	30.3	0.0169
200	29.2	33.6	0.0150
400	31.1	36.5	0.0171
800	33.3	39.2	0.0179
1600	35.1	41.6	0.0186

Table IX.—Conductivity of Lithium Bromide in a Mixture of 25 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	7.26	9.32	0.0283
50	9.49	12.23	0.0289
100	10.00	12.94	0.0294
200	10.93	14.11	0.0291
400	11.21	14.51	0.0294
800	11.68	15.16	0.0298
1600	12.02	15.72	0.0308

Table X.—Conductivity of Lithium Bromide in a Mixture of 50 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	2.91	4.25	0.0462
50	3.40	4.97	0.0459
100	3.61	5.29	0.0466
200	3.85	5.61	0.0458
400	3.85	5.64	0.0466
800	3.98	5.86	0.0474
1600	4.02	5.89	0.0466

Table XI.—Conductivity of Lithium Bromide in a Mixture of 75 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	0.947	1.62	0.0710
50	1.08	1.85	0.0711
100	1.14	1.95	0.0719
200	1.14	1.95	0.0718
400	1.19	2.06	0.0720
800	1.18	2.02	0.0713
1600	1.25	2.15	0.0724

Table XII.—Conductivity of Lithium Bromide in Methyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	50.0	56.4	0.0127
50	64.3	72.9	0.0134
100	69.4	78.4	0.0129
200	74.1	84.0	0.0134
400	77.4	87.4	0.0129
800	79.9	89.7	0.0124
1600	81.9	93.1	0.0137

Table XIII.—Conductivity of Lithium Bromide in a Mixture of 25 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	21.3	25.8	0.0214
50	25.5	30.9	0.0210
100	27.1	32.9	0.0213
200	28.9	35.3	0.0222
400	29.2	35.7	0.0221
800	30.3	36.8	0.0215
1600	31.2	38.3	0.0226

Table XIV.—Conductivity of Lithium Bromide in a Mixture of 50 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	7.34	9.94	0.0350
50	8.44	11.41	0.0353
100	8.86	11.98	0.0352
200	9.21	12.48	0.0355
400	9.49	12.87	0.0356
800	9.59	13.05	0.0361
1600	9.90	13.44	0.0357

Table XV.—Conductivity of Lithium Bromide in a Mixture of 75 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	1.73	2.78	0.0607
50	2.01	3.21	0.0599
100	2.13	3.38	0.0584
200	2.30	3.38	0.0470
400	..	..	..
800	2.20	3.55	0.0614
1600	2.17	3.49	0.0626

Table XVI.—Conductivity of Cobalt Chloride in Glycerol at 25°, 35°, and 45°.

				Temperature coefficients.	
V.	$\mu_v 25°$.	$\mu_v 35°$.	$\mu_v 45°$.	25°–35°.	35°–45°.
10	0.270	0.546	1.003	0.1023	0.0836
50	0.369	0.744	1.373	0.1015	0.0846
100	0.391	0.784	1.450	0.1004	0.0780
200	0.455	0.911	1.691	0.1004	0.0857
400	0.473	0.959	1.779	0.1027	0.0855
800	0.497	1.005	1.856	0.1011	0.0847
1600	0.519	1.040	1.920	0.1002	0.0846

Table XVII.—Conductivity of Cobalt Chloride in Water at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature. coefficients.
10	168.9	204.7	0.0212
50	195.5	236.8	0.0212
100	204.2	246.7	0.0205
200	212.6	256.5	0.0207
400	219.4	267.9	0.0217
800	226.6	276.9	0.0222
1600	232.6	282.6	0.0216

Table XVIII.—Conductivity of Cobalt Chloride in a Mixture of 25 per cent Glycerol and Water at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	79.9	100.1	0.0252
50	92.6	116.4	0.0258
100	97.6	122.9	0.0259
200	101.7	128.4	0.0262
400	105.3	133.1	0.0264
800	108.5	136.6	0.0260
1600	110.2	139.7	0.0267

Table XIX.—Conductivity of Cobalt Chloride in a Mixture of 50 per cent Glycerol and Water at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	28.8	38.7	0.0346
50	33.7	45.4	0.0346
100	35.4	47.6	0.0346
200	37.1	49.7	0.0340
400	38.1	51.2	0.0344
800	39.4	53.3	0.0352
1600	40.4	54.5	0.0349

Table XX.—Conductivity of Cobalt Chloride in a Mixture of 75 per cent Glycerol and Water at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	5.72	8.82	0.0542
50	6.93	10.64	0.0536
100	7.30	11.22	0.0536
200	7.69	11.87	0.0543
400	7.94	12.22	0.0540
800	8.42	12.95	0.0538
1600	8.33	12.75	0.0531

Table XXI.—Conductivity of Cobalt Chloride in Ethyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	4.71	4.96	0.0053
50	9.19	9.05	—0.0017
100	12.18	11.92	—0.0021
200	15.71	15.54	—0.0011
400	19.56	19.64	0.0004
800	24.07	24.91	0.0034
1600	28.78	30.38	0.0056

Table XXII.—Conductivity of Cobalt Chloride in a Mixture of 25 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	5.43	6.70	0.0233
50	8.13	10.10	0.0243
100	9.30	11.52	0.0239
200	10.66	13.25	0.0243
400	12.14	15.01	0.0236
800	13.89	17.28	0.0244
1600	15.55	19.39	0.0246

Table XXIII.—Conductivity of Cobalt Chloride in a Mixture of 50 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	2.63	3.77	0.0436
50	3.65	5.11	0.0400
100	4.12	5.78	0.0402
200	4.66	6.53	0.0403
400	5.14	7.32	0.0424
800	5.65	8.03	0.0423
1600	5.86	8.46	0.0443

Table XXIV.—Conductivity of Cobalt Chloride in a Mixture of 75 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	0.953	1.58	0.0652
50	1.29	2.11	0.0638
100	1.41	2.32	0.0650
200	1.58	2.63	0.0662
400	1.69	2.81	0.0666
800	1.89	3.14	0.0660
1600	1.89	3.20	0.0662

Table XXV.—Conductivity of Cobalt Chloride in Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	41.9	44.7	0.0066
50	64.6	69.6	0.0077
100	75.6	82.5	0.0098
200	88.9	94.6	0.0065
400	102.2	110.4	0.0080
800	118.1	126.8	0.0078
1600	132.5	144.6	0.0092

Table XXVI.—Conductivity of Cobalt Chloride in a Mixture of 25 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	19.6	23.0	0.0173
50	27.8	32.6	0.0172
100	32.1	37.7	0.0175
200	36.6	43.1	0.0176
400	40.7	48.2	0.0185
800	44.8	53.4	0.0192
1600	48.8	57.4	0.0179

Table XXVII.—Conductivity of Cobalt Chloride in a Mixture of 50 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	7.64	10.01	0.0310
50	10.22	13.64	0.0334
100	11.64	15.37	0.0323
200	12.84	17.07	0.0330
400	14.11	18.77	0.0330
800	14.99	20.17	0.0346
1600	15.41	20.88	0.0355

Table XXVIII.—Conductivity of Cobalt Chloride in a Mixture of 75 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	1.90	3.00	0.0577
50	2.55	3.99	0.0569
100	2.81	4.43	0.0577
200	3.12	4.95	0.0589
400	3.55	5.36	0.0600
800	3.51	5.63	0.0606
1600	3.59	5.76	0.0606

Table XXIX.—Conductivity of Potassium Iodide in Glycerol at 25°, 35°, and 45°.

V.	μ_v25°.	μ_v35°.	μ_v45°.	Temperature coefficients. 25°–35°.	Temperature coefficients. 35°–45°.
10	0.291	0.607	1.189	0.1087	0.0844
50	0.326	0.667	1.275	0.1045	0.0912
100	0.324	0.670	1.257	0.1068	0.0875
200	0.334	0.687	1.284	0.1056	0.0870
400	0.338	0.686	1.282	0.1030	0.0871
800	0.346	0.708	1.325	0.1048	0.0871
1600	0.352	0.717	1.326	0.1039	0.0849

Table XXX.—Conductivity of Potassium Iodide in Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	125.6	150.4	0.0189
50	131.6	156.5	0.0189
100	133.6	159.3	0.0192
200	135.8	162.1	0.0193
400	137.2	163.7	0.0193
800	138.9	165.9	0.0194
1600	140.0	167.5	0.0196

Table XXXI.—Conductivity of Potassium Iodide in a Mixture of 25 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	61.5	76.6	0.0244
50	64.3	80.1	0.0246
100	65.4	81.7	0.0249
200	66.9	83.4	0.0249
400	67.0	83.9	0.0251
800	68.1	85.2	0.0252
1600	68.7	86.0	0.0252

Table XXXII.—Conductivity of Potassium Iodide in a Mixture of 50 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	23.9	30.8	0.0289
50	24.4	32.3	0.0327
100	24.6	32.8	0.0333
200	24.9	33.2	0.0332
400	25.1	33.4	0.0336
800	25.4	34.1	0.0340
1600	25.5	34.5	0.0351

Table XXXIII.—Conductivity of Potassium Iodide in a Mixture of 75 per cent Glycerol and Water at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	4.94	7.66	0.0552
50	5.13	7.98	0.0555
100	5.25	8.18	0.0559
200	5.14	8.01	0.0559
400	5.42	8.50	0.0569
800	5.48	8.56	0.0563
1600	5.20	8.02	0.0545

Table XXXIV.—Conductivity of Potassium Iodide in Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	21.6	24.8	0.0146
50	28.5	32.7	0.0148
100	31.9	36.9	0.0156
200	35.4	41.5	0.0171
400	37.9	44.5	0.0173
800	40.8	48.1	0.0177
1600	42.6	50.3	0.0179

Table XXXV.—Conductivity of Potassium Iodide in a Mixture of 25 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	9.50	12.27	0.0291
50	11.35	14.68	0.0293
100	12.12	15.79	0.0303
200	12.88	16.87	0.0309
400	13.40	17.56	0.0310
800	13.99	18.33	0.0310
1600	14.62	18.70	0.0278

Table XXXVI.—Conductivity of Potassium Iodide in a Mixture of 50 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	3.87	5.67	0.0466
50	4.31	6.31	0.0466
100	..	..	...
200	4.66	6.93	0.0484
400	4.78	7.03	0.0470
800	4.96	7.29	0.0471
1600	4.98	7.28	0.0460

Table XXXVII.—Conductivity of Potassium Iodide in a Mixture of 75 per cent Glycerol and Ethyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	1.19	2.05	0.0723
50	1.19	2.11	0.0770
100	1.33	2.28	0.0717
200	1.39	2.37	0.0707
400	1.42	2.43	0.0709
800	1.46	2.51	0.0709
1600	1.49	2.50	0.0700

Table XXXVIII.—Conductivity of Potassium Iodide in Methyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	65.5	72.9	0.0114
50	79.6	89.1	0.0120
100	84.0	94.1	0.0121
200	90.9	102.1	0.0122
400	94.8	106.6	0.0125
800	98.0	111.2	0.0134
1600	100.8	113.4	0.0125

Table XXXIX.—Conductivity of Potassium Iodide in a Mixture of 25 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	26.4	32.2	0.0219
50	30.6	37.3	0.0220
100	31.8	38.6	0.0218
200	33.3	40.5	0.0217
400	34.2	41.9	0.0224
800	35.3	43.0	0.0218
1600	35.7	44.1	0.0233

Table XL.—Conductivity of Potassium Iodide in a Mixture of 50 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	μ_v25°.	μ_v35°.	Temperature coefficients.
10	9.15	12.5	0.0366
50	10.2	13.9	0.0365
100	10.4	14.2	0.0363
200	10.8	14.8	0.0364
400	11.1	15.1	0.0363
800	11.5	15.6	0.0364
1600	11.8	16.1	0.0364

Table XLI.—Conductivity of Potassium Iodide in a Mixture of 75 per cent Glycerol and Methyl Alcohol at 25° and 35°.

V.	$\mu_v 25°$.	$\mu_v 35°$.	Temperature coefficients.
10	2.08	3.41	0.0635
50	2.28	3.68	0.0619
100	2.39	3.90	0.0635
200	2.35	3.82	0.0624
400	2.40	3.90	0.0631
800	2.56	4.27	0.0663
1600	2.46	4.07	0.0648

Tables IV. to XV. show the conductivities of lithium bromide in various mixtures of glycerol with water, methyl alcohol, and ethyl alcohol. The results are plotted in Figures I., II., and III. The curves show that the conductivities in the mixtures depart widely from the law of averages, there being a marked sagging of the curves in each case. The results are much like those obtained by Jones and Carroll with cadmium iodide in mixtures of water and methyl alcohol. No minimum is observed, nor, indeed, has any minimum appeared in all the work with glycerol solutions. This is not surprising. It is hardly probable that any mixture of glycerol with the less viscous solvents would have a viscosity greater than that of pure glycerol. It is conceivable, however, that a mixture of glycerol with a very small percentage of water or alcohol might give a slight minimum in fluidity, but the difficulty of determining this point would be very great. At the same time, a similar minimum in the conductivity curves might make its appearance, and the parallelism of the two sets of curves, which is one of the points to be established, would not be changed, even if minima were found. At any rate, it is evident that in the case of mixtures of glycerol with the other three solvents used, we have to deal with mixtures of the second class referred to above; that is, mixtures whose properties are not additive.

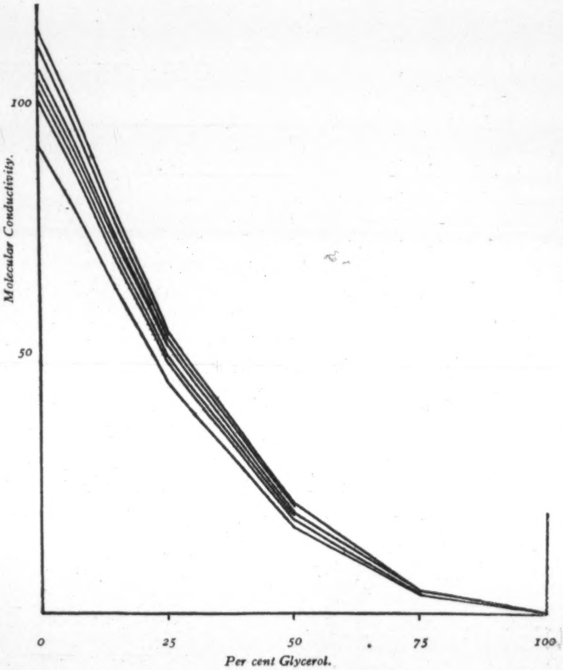


Fig. I.—Conductivity of Lithium Bromide in Glycerol-Water at 25°.

Cobalt Chloride.

The cobalt chloride was first crystallized from conductivity water, to free it from traces of sulphates. The crystallization was continued until the mother liquor no longer clouded barium chloride solution. The salt was then partially dehydrated in a vacuum desiccator, with sulphuric acid, after which it was pulverized, and heated in the air till it had assumed a lavender color. After being again pulverized, it

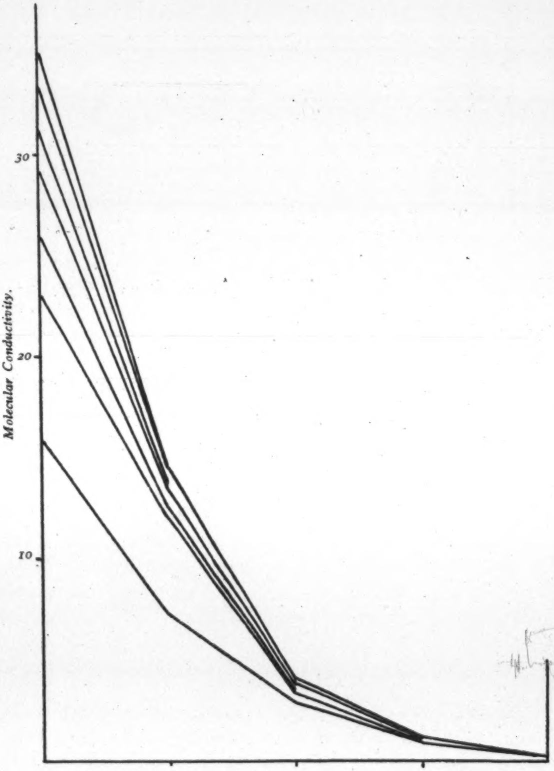


Fig. II.—Conductivity of Lithium Bromide in Glycerol-Ethyl Alcohol at 25°.

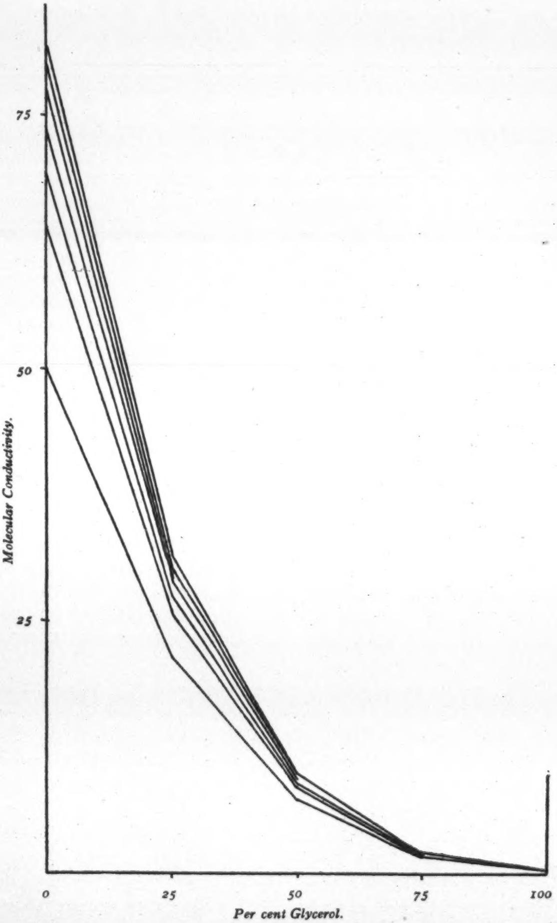


Fig. III.—Conductivity of Lithium Bromide in Glycerol-Methyl Alcohol at 25°.

was placed in a hard-glass tube, and heated in a current of dry hydrochloric acid gas for several hours at 250°, during which process it changed color to a pale pure blue. The hydrochloric acid gas was then replaced by a stream of nitrogen dried over phosphorus pentoxide, and the tube allowed to cool slowly. The cobalt chloride gave a clear solution in water, which, however, when exposed to sunlight, deposited a very small quantity of a flocculent brown precipitate. Not enough of this could be obtained for a complete examination. It did not contain iron, and did not give the reactions of bivalent cobalt. It is thought to be a cobaltic compound, produced by some oxidizing action brought about by the sunlight. Solutions kept in the dark did not show this precipitate, even when allowed to stand overnight; but ten minutes' exposure to bright sunlight was sufficient to cause the change. For this reason, the conductivities of cobalt chloride in aqueous solution are considered a little uncertain, and are probably a little too high. Solutions in the alcohols and in glycerol were perfectly clear, and remained so indefinitely, sunlight having no effect on them.

The conductivities of cobalt chloride are given in Tables XVI. to XXVIII. The conductivities in pure glycerol increase regularly, and are considerably higher than the corresponding values for lithium bromide. This is just what would be expected, if glycerol is a normal dissociating solvent. Cobalt chloride would dissociate into three ions, while lithium bromide would give only two, and the conductivities of the former salt would accordingly be greater.

The results are plotted as curves in Figures IV., V., and VI. The curves are in every respect analogous to those for lithium bromide, except in one minor point, to be seen in Figure V. Here the values of conductivity of cobalt chloride in pure ethyl alcohol are abnormally low (at least for all except the most dilute solutions), considering it is a ternary electrolyte. Lithium bromide, for instance, in the tenth-normal solution in ethyl alcohol, has a molecular conductivity of 15.8 at 25°, and we should expect, other things being equal, that cobalt chloride would give a value about 50 per cent greater than

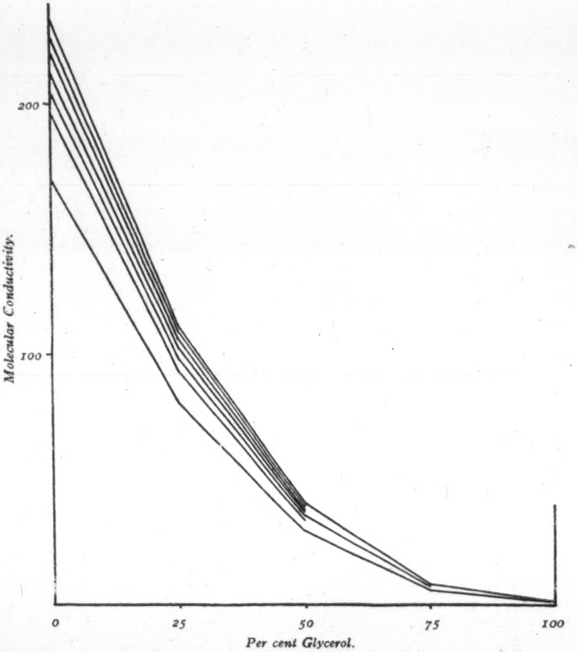


Fig. IV.—Conductivity of Cobalt Chloride in Glycerol-Water at 25°.

this. The value of $\mu_v 25^\circ$ for cobalt chloride in ethyl alcohol is, however, only 4.71. But knowing that many of the halides of the heavy metals tend to form complexes when dissolved in organic solvents, it was suspected that these low results, at least in the concentrated solutions, were due to partial polymerization of the cobalt chloride molecules. This point was kindly tested for us by Mr. H. R. Kreider. He showed by the boiling point method that the dissociation of cobalt chloride in ethyl alcohol, for concentrations ranging near

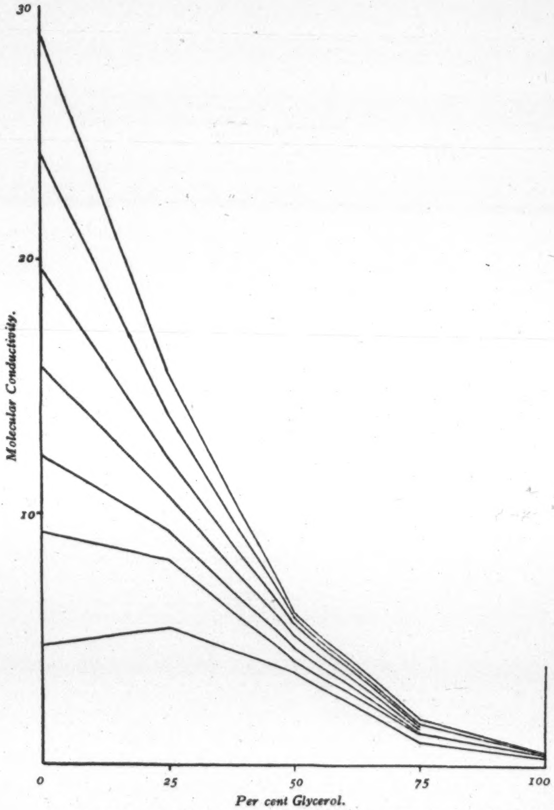


Fig. V.—Conductivity of Cobalt Chloride in Glycerol-Ethyl Alcohol at 25°.

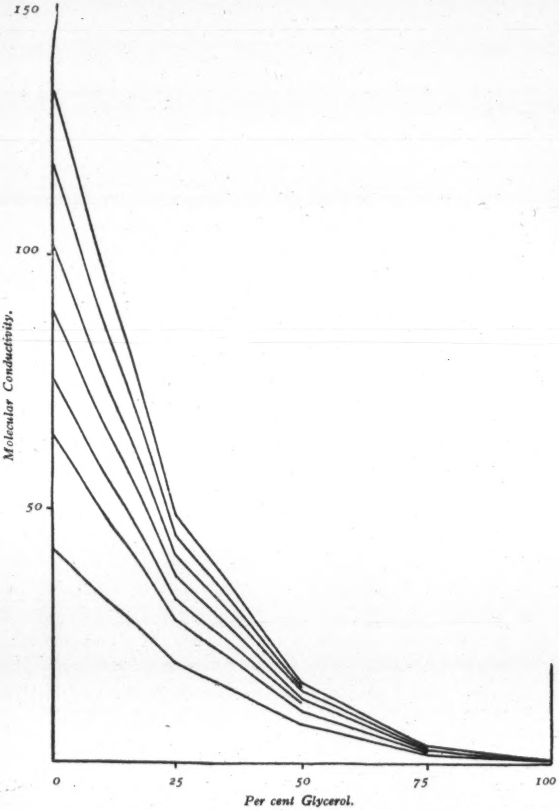


Fig. VI.—Conductivity of Cobalt Chloride in Glycerol-Methyl Alcohol at 25°.

tenth-normal, is apparently negative; or, in other words, the indicated molecular weight is greater than that calculated for $CoCl_2$. Some of his results are given here.

M. W. = 129.96.

Volume.	M. W. found.
8.1	155
13.0	134
13.3	131

The association appears in all three solutions, and since most other salts are dissociated 20 to 30 per cent in ethyl alcohol at these concentrations, we may consider the low conductivity of cobalt chloride in this case to be due to this cause. The same thing is shown in methyl alcohol solutions. The value of $\mu_v 25°$ for lithium bromide in tenth-normal solution is 50.0, against a corresponding value of 41.9 for cobalt chloride. The difference is not so striking here, probably because methyl alcohol is a stronger dissociant than ethyl alcohol.

Potassium Iodide.

Kahlbaum's pure potassium iodide was recrystallized, and dried to constant weight at 150°. It showed no appreciable impurity.

Tables XXIX. to XLI. give the conductivities of potassium iodide in glycerol, and in the mixed solvents. Again, the conductivities increase nearly regularly with dilution, and are a little higher than those of lithium bromide, and about 50 per cent less than the conductivities of cobalt chloride, as we should expect. The results in the mixtures are represented in Figures VII., VIII., and IX., and are in every respect like those obtained for the other two salts. The conductivities are less than the averages in each case.

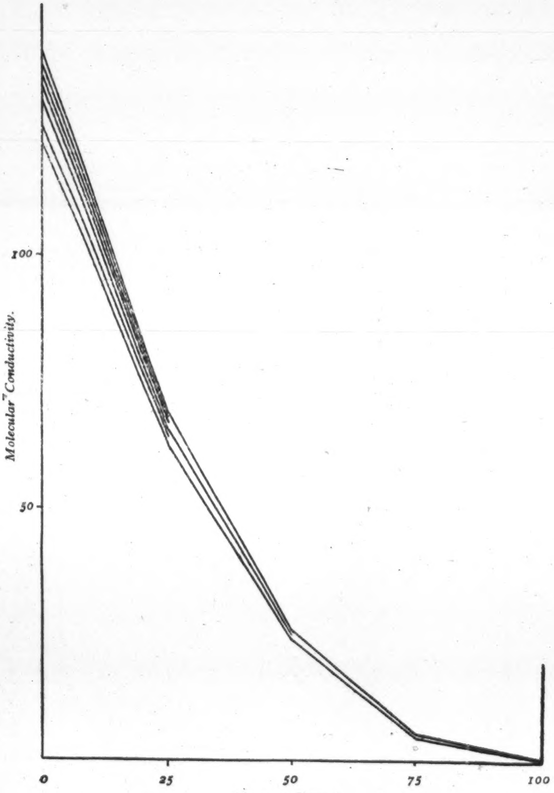


Fig. VII.—Conductivity of Potassium Iodide in Glycerol-Water at 25°.

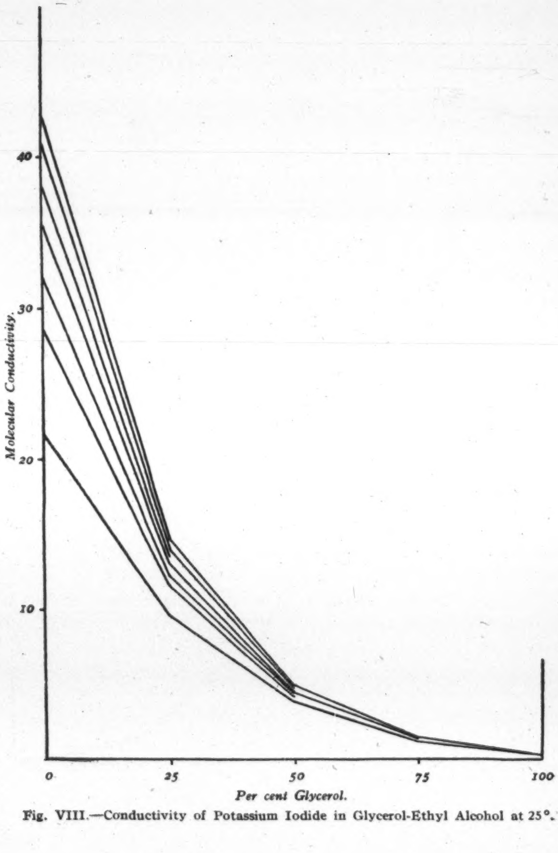


Fig. VIII.—Conductivity of Potassium Iodide in Glycerol-Ethyl Alcohol at 25°.

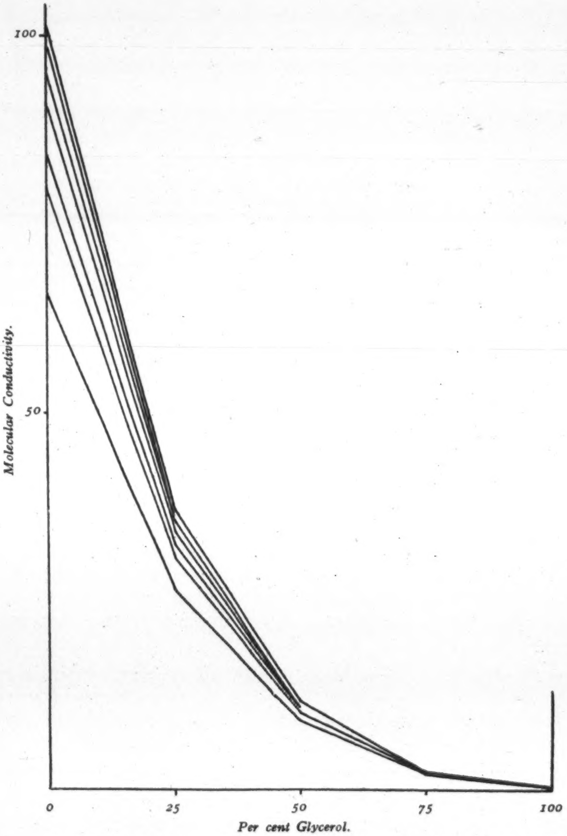


Fig. IX.—Conductivity of Potassium Iodide in Glycerol-Methyl Alcohol at 25°.

Temperature Coefficients of Conductivity.

The most interesting features in this connection are the *very large temperature coefficients of conductivity of the solutions in pure glycerol.* In tenth-normal solution, these are for lithium bromide, cobalt chloride, and potassium iodide, respectively, 10.6 per cent, 10.23 per cent and 10.87 per cent between 25° and 35°, and 8.71 per cent, 8.36 per cent, and 8.44 per cent between 35° and 45°. *These are much the largest temperature coefficients of conductivity thus far observed between these temperatures, and they are closely related to the temperature coefficients of fluidity.*

In the solutions of cobalt chloride in ethyl alcohol, *negative temperature coefficients* of conductivity occur. These have also been noticed by Jones and McMaster in certain solutions of the same salt in mixtures of acetone and the alcohols. In the present case, the temperature coefficient of the tenth-normal solution is positive, though very small, and in the fiftieth-normal solution it becomes negative. The temperature coefficients reach a minimum in the hundredth-normal solution, and then increase regularly, again becoming positive in the dilute solutions. Temperature coefficients of conductivity in ethyl alcohol are always small, and it is known that the degree of ionization decreases with rising temperature. We have already proved that cobalt chloride in ethyl alcohol has a strong tendency to polymerize. The occurrence of negative temperature coefficients of conductivity, therefore, shows that the decrease in ionization, due to rise in temperature, is more than sufficient to overcome the effect of increased ion velocity, brought about by increased fluidity.

In the mixed solvents, the temperature coefficients of conductivity in no case follow the law of averages, but, like the conductivities, are always less than the calculated values.

We have thus shown that for solutions in mixtures of glycerol with water or the alcohols, the molecular conductivities are always less than the averages calculated from the conductivities in the component solvents. Hence, we may conclude that glycerol is a solvent which, when mixed with another, gives a mixture whose properties are not additive, and in this respect glycerol resembles water. In the three cases tested, glycerol causes some change in the state of molecular aggregation of the other solvents, producing mixtures similar, in many ways, to mixtures of water with the alcohols or acetone. We can now proceed to show that the departure from the law of averages is just as pronounced when we examine the fluidities of the mixtures of glycerol.

Table XLII.—Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Water at 25° and 35°.

Water.

Solution.	η 25.	η 35.	ϕ 25.	ϕ 35.	T. C. ϕ.
LiBr	0.009011	0.00723	110.99	138.33	0.0246
$CoCl_2$	0.009209	0.00745	108.58	134.26	0.0237
KI	0.008847	0.007191	113.02	139.06	0.0231
Solvent	0.00891	0.00720	112.25	138.89	0.0237
25 Per Cent Glycerol and Water.					
LiBr	0.02064	0.01552	48.45	64.44	0.0330
$CoCl_2$	0.02156	0.01624	46.49	61.65	0.0326
KI	0.01991	0.01509	50.23	66.25	0.0319
Solvent	0.02003	0.01518	49.91	65.86	0.0319
50 Per cent Glycerol and Water.					
LiBr	0.06246	0.04346	16.01	23.01	0.0437
$CoCl_2$	0.06659	0.04632	15.02	21.59	0.0438
KI	0.06060	0.04252	16.50	23.52	0.0425
Solvent	0.06145	0.04272	16.27	23.41	0.0438
75 Per cent Glycerol and Water.					
LiBr	0.3330	0.2020	3.003	4.949	0.0647
$CoCl_2$	0.3645	0.2202	2.743	4.541	0.0656
KI	0.3246	0.1982	3.081	5.046	0.0638
Solvent	0.3203	0.1954	3.122	5.118	0.0639

Table XLIII.—Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Ethyl Alcohol at 25° and 35°.

Ethyl Alcohol.

Solution.	η 25.	η 35.	ϕ 25.	ϕ 35.	T. C. ϕ.
LiBr	0.01235	0.009864	80.92	101.37	0.0253
$CoCl_2$	0.01193	0.009828	83.80	101.75	0.0214
KI	0.01177	0.00960	84.95	104.16	0.0226
Solvent	0.01110	0.009068	90.07	110.28	0.0224

25 Per cent Glycerol and Ethyl Alcohol.					
LiBr	0.04574	0.03305	21.86	30.26	0.0384
$CoCl_2$	0.04919	0.03612	20.33	27.69	0.0362
KI	0.0452	0.03290	22.12	30.39	0.0374
Solvent	0.04367	0.03188	22.90	31.37	0.0370
50 Per cent Glycerol and Ethyl Alcohol.					
LiBr	0.2275	0.1413	4.515	7.075	0.0588
$CoCl_2$	0.2449	0.1569	4.084	6.375	0.0561
KI	0.2059	0.1327	4.856	7.537	0.0552
Solvent	0.2053	0.1323	4.871	7.559	0.0552
75 Per cent Glycerol and Ethyl Alcohol.					
LiBr	1.193	0.6455	0.8382	1.549	0.0848
$CoCl_2$	1.353	0.7381	0.7391	1.355	0.0833
KI	1.1005	0.6038	0.9089	1.656	0.0822
Solvent	1.0842	0.5971	0.9223	1.675	0.0816

Table XLIV.—Viscosity and Fluidity of Solutions in Mixtures of Glycerol and Methyl Alcohol at 25° and 35°.

Methyl Alcohol.

Solution.	η 25.	η 35.	ϕ 25.	ϕ 35.	T. C. ϕ.
LiBr	0.006097	0.005305	164.01	188.52	0.0149
$CoCl_2$	0.006365	0.005404	157.10	181.65	0.0135
KI	0.005942	0.005149	168.31	194.21	0.0154
Solvent	0.005654	0.004918	176.86	204.59	0.0149
25 Per cent Glycerol and Methyl Alcohol.					
LiBr	0.02105	0.01647	47.51	60.72	0.0279
$CoCl_2$	0.02247	0.01735	44.51	57.64	0.0295
KI	0.02019	0.01588	49.52	62.98	0.0272
Solvent	0.01962	0.01539	50.97	64.97	0.0274
50 Per cent Glycerol and Methyl Alcohol.					
LiBr	0.1012	0.06945	9.882	14.40	0.0458
$CoCl_2$	0.1080	0.07451	9.258	13.42	0.0450
KI	0.0936	0.06353	10.68	15.54	0.0474
Solvent	0.0928	0.06379	10.78	15.68	0.0454
75 Per cent Glycerol and Methyl Alcohol.					
LiBr	0.6525	0.3803	1.532	2.630	0.0717
$CoCl_2$	0.7379	0.4165	1.352	2.401	0.0776
KI	0.6288	0.3637	1.590	2.750	0.0729
Solvent	0.6073	0.3552	1.647	2.815	0.0709

Table XLV.—Viscosity and Fluidity of Solutions in Glycerol at 25° and 35°.

Solution.	η 25.	η 35.	ϕ 25.	ϕ 35.	T. C. ϕ.
LiBr	6.786	3.192	0.1474	0.3133	0.1126
$CoCl_2$	7.530	3.364	0.1328	0.2973	0.1261
KI	6.723	3.139	0.1487	0.3186	0.1143
Solvent	6.330	2.9403	0.1580	0.3401	0.1153

Viscosity and Fluidity.

Tables XLII. to XLV., inclusive, give the viscosities and fluidities of the pure solvents, the mixed solvents, and the tenth-normal solutions of the three salts in these liquids. The fluidities of the solutions are, as usual, in nearly every case less than those of the corresponding solvents. In three solutions, however, we have the phenomenon of negative viscosity. These are potassium iodide in water, and in 25 and 50 per cent glycerol and water, at both 25° and 35°. An explanation of negative viscosity has been given by Jones and Veazey.[1] It is interesting to find that the fluidity of even so immobile a liquid as 50 per cent glycerol and water is increased by the addition of potassium iodide. In the 75 per cent mixture, the viscosity coefficient is again positive, but the difference between the viscosity of the mixture and of tenth-normal potassium iodide in it is not great. The salt does not lower the viscosity of pure glycerol, nor of any of the other solvents used.

But if we examine the viscosities of the solutions in pure glycerol, we see that the effect of the several salts on the viscosity of the solvent is in inverse ratio to the molecular volumes of the salts. Potassium iodide, with the largest molecular volume, increases the viscosity of glycerol less than does lithium bromide, which has a slightly smaller molecular volume. The latter salt, in turn, increases the viscosity of glycerol much less than does cobalt chloride, which has much the smallest molecular volume of the three. *Relations exactly analogous to these* have been pointed out by Jones and Veazey, and the mechanism of the effect has been sufficiently discussed in the first part of this work.

[1] This Journal, **37**, 405 (1907).

The viscosity of pure glycerol at 25°—6.330—is 1120 times that of methyl alcohol at the same temperature. A wide range of viscosity has thus been covered, yet the same relations hold as obtain in mixtures of the much more fluid solvents studied by Jones and his coworkers The fluidities at 25° are plotted as curves in Fig. X. Curve I. represents the fluidities of glycerol-methyl alcohol mixtures, curve II. represents glycerol-water, and curve III. represents glycerol-ethyl alcohol. The curves resemble the conductivity curves very closely, show the same sagging, and have no minima.

The temperature coefficient of fluidity of pure glycerol between 25° and 35° is 11.53 per cent, and this is very nearly equal to the temperature coefficients of conductivity of the salts used in this work. In all the solutions, the temperature coefficient of fluidity is greater than the temperature coefficients of conductivity, as has been observed in practically all cases heretofore. This is probably due partly to the decrease of dissociation with rising temperature.

It will be seen that in the majority of cases, the temperature coefficient of fluidity of any solution is slightly greater than that of the solvent. As is known, dissociation decreases slightly with rising temperature. This would cause the solution at higher temperature to contain a greater number of whole molecules, whose volume would be equal to that of their component ions, but whose frictional surfaces would be less. This would decrease the total frictional surface of the particles in the solution, and an increase in the fluidity would result, in addition to that caused by the ordinary increase in the fluidity of the pure solvent. This relation does not hold for all of the temperature coefficients of fluidity, but the exceptions are not many, and it would seem that an explanation like the above is at least partially correct.

A comparison of the conductivity and fluidity curves shows, then, that the two phenomena, in mixtures of glycerol with water or the alcohols, are very closely parallel. No minima are found, but every curve shows a falling below the straight line of averages. Hence, we must conclude that glycerol is a solvent resembling water more closely than it does the

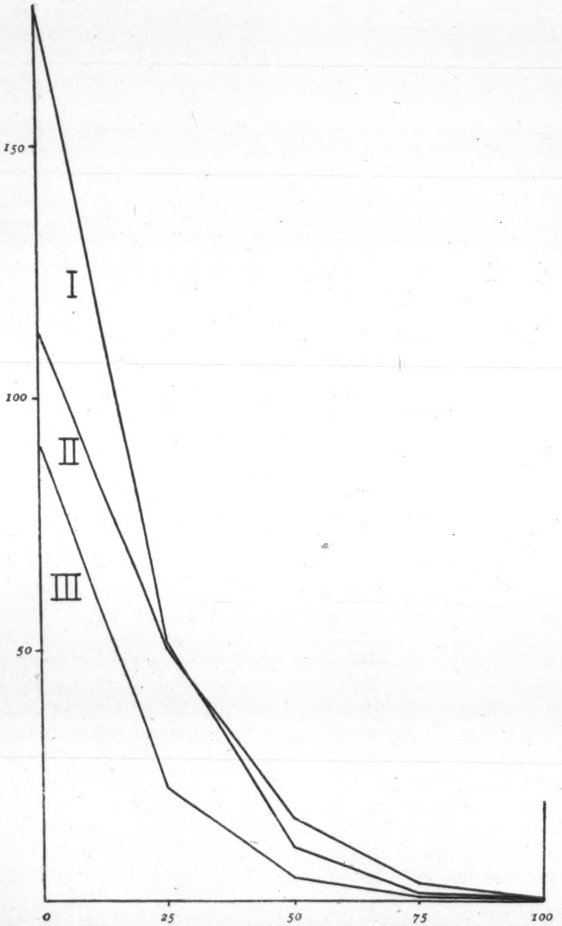


Fig. X.—Fluidities of Glycerol Mixtures at 25°.

alcohols, in that mixtures containing it do not have additive properties. This resemblance to water comes out more strikingly when we examine the relative values of the conductivities of the three salts studied here, in the different pure solvents. In water, cobalt chloride, being a ternary electrolyte, has a greater conductivity than potassium iodide, and potassium iodide again has a conductivity greater than lithium bromide. The same order is found in glycerol. In ethyl alcohol and in the tenth-normal solutions in methyl alcohol, the order is potassium iodide, lithium bromide, cobalt chloride. We have already shown that cobalt chloride in ethyl alcohol forms complexes. It is evident that in glycerol the same salt does not form complexes, but behaves like a normal ternary electrolyte in a strongly dissociating solvent. It seems to be broken down, at least partly, into three ions, even in the fairly concentrated solutions in glycerol, and in this point the latter resembles water rather than the alcohols.

The conductivities of the several electrolytes in pure glycerol do not reach limiting values in the dilutions worked with here, but the conductivities for dilutions of four-hundredth-normal and more are increasing very slowly; in other words, complete dissociation is probably reached in glycerol solutions at a comparatively small volume. This feature again recalls the dissociating action of water.

If we multiply 0.35, the highest conductivity obtained for potassium iodide in glycerol at 25°, by 6.330, the viscosity of the solvent at that temperature, the product is 2.22. Similarly, at 35° the product is 2.10. These numbers, nearly identical, represent lower limits, so to speak of the product $\mu_\infty \eta$ for glycerol. It will be recalled that Walden found this value to be nearly a constant, independent of temperature, for about thirty organic solvents. Water and glycol, with values equal to 1.0 and 1.32 respectively, were exceptions. Glycerol thus becomes another exception, with a product of at least 2.10. If we compare methyl alcohol, the simplest monacid carbinol, with glycerol, the simplest diacid carbinol, and with glycerol, the simplest triacid carbinol, we see that conductivity does not increase proportionately to fluidity, but to some fractional power of fluidity.

Solvent.	$\mu_\infty \eta$.
CH_3OH	0.72
$C_2H_4(OH)_2$	1.32
$C_3H_5(OH)_3$	2.10

A similar conclusion has been drawn by Green[1] from a study of the conductivity and viscosity of solutions of lithium chloride in water containing various amounts of sucrose, and he finds that $\mu_\infty = K\phi^{0.7}$.

Summary of Facts Established.

(1) Glycerol, with water, or with methyl or ethyl alcohol, forms binary mixtures whose properties are not additive.

(2) The conductivity curves of three electrolytes in these mixtures in no case obey the law of averages.

(3) The same is true of the fluidity curves.

(4) The temperature coefficients of conductivity of solutions in pure glycerol are very large, and nearly identical with the temperature coefficients of fluidity.

(5) Glycerol, as a dissociating liquid, resembles water more closely than it does the alcohols.

(6) Conductivity increases with fluidity, but instead of increasing at the same rate, varies as some fractional power of fluidity.

Physical Chemical Laboratory,
Johns Hopkins Univ.,
Baltimore, May, 1909.

REVIEWS.

Die Lagerung der Atome im Raume. Von J. H. van't Hoff. Dritte umgearbeitete und vermehrte Auflage, mit 24 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. pp. 147. 1908. Price, M. 4.50.

This work by van't Hoff is one of his three or four epoch-making contributions to chemistry. Indeed, it may be fairly said that the contributions of van't Hoff to the general subject of stereochemistry, or the positions of the atoms in space in organic compounds, have furnished the philosophy for organic chemistry for the last quarter of a century.

---

[1] J. Chem. Soc., **93**, 2049 (1908).

The preface to the first edition of this little book was written in 1876 by Johannes Wislicenus, then in Würzburg.

The preface to the second edition was written in 1894, by the same chemist who was then in Leipzig, and from whose laboratory so much of importance was contributed to this subject.

This splendid man is now gone, and van't Hoff writes his own brief preface to the third edition in 1908.

Although the work is so well known to mature chemists, it may not be as familiar to the younger men. A brief reference to its contents may, therefore, not be out of place. The first nine chapters are devoted to the stereochemistry of carbon: The asymmetric carbon atom; Compounds with several asymmetric carbon atoms; Ring union; Preparation of isolated antipodes; Determination of position in stereoisomers; Transformation of optical antipodes; Double and triple union in carbon compounds; and The numerical value of the rotatory power.

The second part of the book is devoted to the stereochemistry of elements other than carbon, including sulphur, selenium, tin, silicon, and optical isomerism in the case of pentavalent nitrogen.

The new edition brings the subject up-to-date, and like any contribution from the pen of van't Hoff, will be most heartily welcomed to the chemical world. No chemist can afford to be without a copy of the newest edition of this book.

H. C. J.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemistry in Columbia University. Fourth edition, revised and enlarged. New York: John Wiley and Sons; London: Chapman and Hall, Limited. 1908. pp. XIV + 539. Price, $3.

To those familiar with the previous editions[1] of this interesting book, the scope of this new edition is indicated by the words of the author: "All the changes made in this edition have been undertaken with the view of bringing the subject matter up to date and making the various relations more intelligible to the average nonmathematical, reader .... The sections on 'indicators' and 'general analytical reactions' have been omitted, for they are now presented in all the better text-books on analytical chemistry."

It is surprising how much is told in this little volume. There is scarcely a paragraph that is not packed with information and the range of topics discussed is remarkably wide. Too often the chemist finds physico-chemical methods as presented unintelligible and therefore useless. In this book, however, we find remarkably clear presentation and numerous examples of the practical application of the methods described. A great many calculations are explained throughout the text and a large number of problems is subjoined.

---

[1] See THIS JOURNAL, **21**, 459; **28**, 242; **34**, 593.

The writer follows Ostwald in dispensing with the atomic and molecular hypotheses. This seems of doubtful advisability in a text-book of "elements" in view of the fact that the objections to these hypotheses are purely philosophical. It certainly does not aid the comprehension of the average student to dispense with such excellent tools unless some better ones are offered.

The use of the term "chemical energy" (p. 426 ff.) is rather ambiguous from a thermodynamic standpoint, meaning, as the author does, change in total energy and not free or reaction energy. On p. 442 the electromotive force of a calomel electrode is misprinted as —0.0613 instead of —0.613.

Any objections, however, are of minor importance, and this new edition will prove a valuable book for students of the subject.

JOEL H. HILDEBRAND.

QUALITATIVE ANALYSE VOM STANDPUNKTE DER IONENLEHRE. VON DR. WILHELM BÖTTGER, Privatdozent und Oberassistent am Phys.-chem. Institut der Universität Leipzig. Zweite, umgearbeitete und stark erweiterte Auflage. Mit 24 Figuren im Text, einer Spektraltafel und besonderen Tabellen zum Gebrauche im Laboratorium. Leipzig: Verlag von Wilhelm Engelmann. 1908. pp. 524.

The first edition of this admirable book by Dr. Böttger is very well known. A large amount of work has been expended in revising it, and to good purpose. The author tells us that a year of strenuous toil has been devoted to the preparation of the second edition.

This work deals with the subject of qualitative analysis, not in the empirical manner in which it was taught a comparatively few years ago, but from the standpoint of the epoch-making generalizations of the newer physical chemistry. Under "Fundamental Principles," the ionic theory, valence, reversible reactions, the law of mass action, hydrolysis, amphoteric electrolytes, oxidation and reduction, colloids, catalyzers, etc., are considered; and it will be recognized that these principles lie right at the basis of chemical science.

A large section of the book discusses the characteristic reactions of the cations or metals, and still another the characteristic reactions of the anions or acid radicals.

The usual tests for cations and anions in terms of the several groups, together with preliminary tests, are considered at length.

The book contains a fairly large section devoted to the rare earths which is of unusual interest and importance. The so-called rare earths are many of them no longer rare, and all of them have acquired a special interest in the last few years, due especially to the work of the Welsbach Light Co., which has separated many of these substances in large quantities. The methods for separating these substances are discussed at length.

All in all, this is easily our most modern and scientific treatise on the subject of qualitative analysis. H. C. J.

GENERAL CHEMISTRY FOR COLLEGES. By ALEXANDER SMITH, Professor of Chemistry and Director of General and Physical Chemistry in the University of Chicago. New York: The Century Co. 1908. pp. 529.

Professor Smith's "General Inorganic Chemistry"[1] is marked by an excellent arrangement of theory and fact, with more physical-chemical theory than is found in any other text-book of inorganic chemistry, and also by proper sequence and great clearness.

The "General Chemistry for Colleges" is written on the same plan. It contains less theory than the large book, but what is given is developed very fully; it is much simpler and better fitted for college students. Although much of the matter of the larger book is retained in this, there is so much that is quite new in treatment, that it can not be regarded as an abridgement of the larger work.

This book deserves the success with beginners that the larger book has with older students. E. R.

A TEXT-BOOK OF BOTANY AND PHARMACOGNOSY. By HENRY KRAEMER, PH.B., PH.D., Professor of Botany and Pharmacognosy, and Director of the Microscopical Laboratory, in the Philadelphia College of Pharmacy. Third edition, revised and enlarged. Illustrated with over 300 plates comprising about 2000 figures. J. B. Lippincott Co. Philadelphia. pp. 850.

As is indicated in the sub-title this book is intended for students of pharmacy, as a reference book for pharmacists, and as a hand-book for food and drug analysts. Since the first edition in 1902, this book has more than doubled in size and corresponding usefulness and now contains 850 pages.

---

[1] THIS JOURNAL, **36**, 217.

The subject matter is divided into three parts: I. Botany. II. Pharmacognosy. III. Reagents and Microscopical Technique. The first part occupies about one-half the book and in it the main facts on classification, morphology, and histology are given in a manner which should make it interesting and instructive to pharmacy students.

In the second part the principal official and nonofficial drugs are described. Many cuts accompany the descriptions, illustrating the drug structure. The chapter on powdered drugs is also well illustrated, many of the cuts being original, others taken from such well-known sources as Meyer, Moeller and Vogl. A key for the identification of vegetable powders is given, which makes this part especially valuable to pharmacists who use the microscope.

The press work on the book is excellent and it should prove a valuable addition to the library of the food and drug analyst and pharmaceutical student.

PRINCIPLES AND PRACTICE OF AGRICULTURAL ANALYSIS. Vol. II. By HARVEY W. WILEY, A.M., PH.D., Chief of the Bureau of Chemistry, U. S. Department of Agriculture, Washington, D. C. Second edition, revised and enlarged. The Chemical Publishing Co., Easton, Pa. pp. 680.

This volume is more than twice the size of the corresponding volume of the first edition.

Much of the material relating to ammonia, nitrous and nitric acid, which appeared in the first volume of the first edition, has been rewritten and transferred to this volume.

This work is unlike that frequently seen in "second editions" for the reason that the volume has been most carefully and conscientiously rewritten, enlarged, and brought up to date.

The new features are: a description of the processes employed in combining atmospheric nitrogen in the manufacture of calcium cyanamide and calcium nitrate; a résumé of the experiments thus far made for the purpose of determining their agricultural value; and the introduction of methods for the examination and analysis of fungicides and insecticides.

Part first opens with a general discussion, followed by a description of methods for sampling all classes of materials preparatory to analysis. This part is devoted primarily to a discussion of phosphates in all of their relations, such as occurrence, origin, associated ingredients, agricultural utilization, and chemical analysis.

Part second is devoted to natural and artificial nitrogenous compounds and the analytical methods employed in their analysis in many of the leading countries of the world.

Part third is devoted to a review of the origin, extent, and utilization of the great deposits of potassium salts in Germany, to a discussion of other sources of potash, and to the various analytical methods for its determination.

Part fourth embraces a discussion of miscellaneous fertilizers; also of insecticides, fungicides, and methods for their analysis.

In considering methods of analysis not only those now in use but most of the earlier methods of prominence are discussed. Frequent mention is made of the advantages or disadvantages which certain methods afford. In view of this feature and on account of the general fund of information relating to the origin, methods of manufacture, and utilization of many of the materials which are discussed, the work is made indispensable not only to the ordinary analyst, but also to agricultural and manufacturing chemists and students of agriculture.

One might take exception to the high tribute paid to natural iron and aluminum phosphates as fertilizers; possibly also undue prominence is given to the discussion of the manurial value of finely pulverized feldspar, and such reference as "no claim has been made that ground feldspar is an efficient substitute, under all circumstances, for potash salts," seems likely to lead to undue expectations as to its efficiency.

Apparently few errors, oversights, or important omissions have occurred, which is perhaps exceptional for so large a volume, prepared by a single author.

But few other recent writers have had the good fortune to render the chemists of the United States and of the entire world so largely their debtors.

H. J. WHEELER.